BOOK of ABSTRACTS

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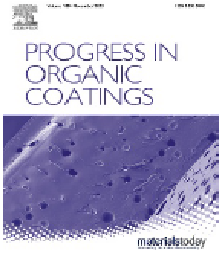
POLYMER CHEMISTRY IS SPONSOR OF ESPS 2024 by supporting 3 awards for the 3 best Poster	Journal PROGRESS IN ORGANIC COATINGS IS SPONSOR OF ESPS 2024 by supporting 1 Awards for the best Lecture 
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ABSTRACTS

PREFACE

Dear Colleagues and friends,

It is with great pleasure and excitement that I extend to all of you a warm welcome to the 8th European Symposium of PHOTOPOLYMER SCIENCE, which is held in Stresa, Italy.
As we gather together, we embark on a journey of exploration, discovery, and collaboration that promises to shape the landscape of our collective knowledge in the field of photopolymerization. These days will give us the power of shared inquiry and the exchange of ideas. It will serve as a platform for thinkers, innovators in the field of photopolymerization.
Photopolymer science and applications is witnessing a continued increase of interest both in academic research as well as in industrial applications because of numerous environmental and economic benefits of light induced polymerization processes.
We will listen about photochemistry, advancement in photoinitiators, radical and cationic UV-Curing, 3D-printing, exploitation of biobased monomers in photopolymerization and the applications of UV-Cured networks in energy, and in biomedical filed.

But beyond the presentations and panel discussions, this conference series is also about fostering connections between individuals. It is about building bridges across boundaries and cultivating a sense of community and mutual respect. As a matter of fact, ESPS meeting has always been like a family reunion. A moment to meet with members of the family coming from different corner of the world, from Europe, from the USA, from Australia, from China, from Japan.
The first ESPS meeting was held in Mulhouse, France in 2010 and the second meeting took place in Torino, Italy in September 2012. In 2014 this conference was held in Vienna with nearly 300 participants. Leipzig continued this successful series in 2016. Then, it came back to Mulhouse 2018. The planned continuation in 2020 was stopped because of corona virus worldwide conditions. In 2021 we organized a virtual ESPS symposium and went back to a face-to-face meeting in 2022 in Istanbul. It is now the turn of Italy to host this important event.

The European Symposium of Photopolymer Science (ESPS) aims to bring together the brightest minds from both academia and industry to collectively present and discuss the more recent innovations in fundamental issues as well as industrial innovations. The meeting consists of seminars with topics addressing critical issues such as photochemistry, reaction kinetics, analytical methods, photoinitiator and monomer synthesis, structure-property relations, polymer processing, as well as applications. I think we put together a wonderful program. We have 12 outstanding invited lectures: 80 regular oral presentations and 52 poster presentations.
As we embark on this journey together, let us embrace the spirit of curiosity, open-mindedness, and collaboration. Let us approach each session with a sense of curiosity and a willingness to challenge our assumptions, expand our horizons, and embrace the novelty in photopolymer science and technology.

Enjoy reading the Book of Abstact where all the novelties that we will listen during the conference are collected. Enjoy the conference in Stresa.

On behalf of ESPS Board Committee
Marco Sangermano

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The Precision Photochemistry Paradigm

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Over the last decade our laboratory has employed monochromatic tunable laser systems to reveal a strong mismatch between the absorptivity of a chromophore and its photochemical reactivity in the vast majority of covalent bond forming reaction as well as specific bond cleavage reactions. Our data overturns the long-held paradigm that effective photochemical reactions are obtained in situations where there is strong overlap between the absorption spectrum and the emission wavelength under a given set of reaction conditions. However – as we explore herein – the absorption spectrum of a molecule provides only information about singlet excitation and remains largely silent on the accessibility of the critical triplet states, which dictate photochemical reactivity. We propose future avenues of enquiry on how photochemical action plots can be understood and demonstrate how they are of key importance for tailoring photochemical applications in soft matter materials design – including in advanced 3D printing and photoresponsive macromolecular systems – with never before seen precision, exploiting wavelength orthogonal, synergistic, cooperative and antagonistic photochemical reaction modes.

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The Scope of Bayfol Hx® Films for Holographic Recordings and its Photochemistry at a Glance

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Bayfol® HX photopolymer films are available as easy-to-process recording materials for volume holographic optical elements (vHOEs).[1] Their recording capabilities from 450 – 850 nm and replay even in a lager spectral range are two of their major advantages. Moreover, the adjustable diffraction efficiency, tunable angular and spectral selectivity of vHOEs recorded into Bayfol® HX as well as their unmatched post-bleaching optical clarity enables superior invisible “off Bragg” optical functionality. As a film product, the replication of vHOEs in Bayfol® HX can be carried out in a highly cost-efficient and purely photonic roll-to-roll (R2R) process. Other supply forms can be considered as well.

Based on a proprietary chemical toolbox, Bayfol® HX can be adopted for a variety of optical applications. We will describe this class of holographic photopolymers and the many photochemistry aspects to build a light-sensitive material in detail, and the chemical response that is based on a reaction-driven diffusion process. Herein, two-component photo initiating systems are especially efficient to photo-polymerize in the visible spectrum. They typically consist of a sensitizer dye that absorbs light and a co-initiator that interacts with the dye to form the initiating species. The initiation mechanism of the radical chain formation involves a photo-induced electron transfer forming the initiating radicals. The chemical energy of the monomers is ideally fully transferred into the targeted refractive index modulations that ultimately form the holographic pattern.

After recording the vHOE, it is necessary to finally bleach and cure any residuals to obtain a highly transparent material (off-Bragg). A combination of light sources can be used to bleach and cure the photopolymer, insights into the photochemical pathways of the former dye molecules will be explained.

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High Throughput, Laser-based Additive Manufacturing of High-Performance Photopolymers

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Laser based additive manufacturing via photopolymerization has gained relevance for high-mix, low-volume production. Toolless fabrication of freely shaped polymer parts offers increased agility in manufacturing compared to traditional methods. Recent advances in photopolymer chemistry have significantly narrowed the gap between 3D printed polymer parts and their injection molded counterparts. However, for mass production with feature resolution < 50 µm, the lack of throughput of high accuracy systems is holding back a broader adoption of additive manufacturing. Fast curing of high-performance resins combined with excellent resolution needs to be realized.

For additive manufacturing, scanning systems based on diode lasers offer unique advantages over conventionally used solid state lasers. Their fast modulation and high beam quality, in the relevant power range typically required for stereolithography (SLA), allow the production of precise polymer parts. However, the material portfolio which conventionally can be used on such SLA systems is limited to resins which can be processed at room temperature. By introducing Hot Lithography[1], laser-based additive manufacturing through controlled heating of a thinly coated material film, a dramatically expanded process window is provided. This expanded window of opportunity for material development represents a unique pathway for innovative photopolymer concepts and gives critical control over the polymerization kinetics, thus influencing network formation and final material properties. Approaching this opportunity by simultaneously satisfying optical as well as chemical limitations opens the gate toward high performance materials with optimized molecular weight, high melting temperatures, strong intermolecular forces, new reactive groups or high contents of functional fillers (e.g., ceramic, metal or polymer)[2,3].

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One-Component Cationic Photoinitiators Based Ion Coumarin Scaffold Iodonium Salts as Highly Sensitive Photoacid Genera 3d-Vat Printing Nanocomposite Photopolymers

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Coumarin and its derivatives gain great interest in the field of photochemistry, due to their properties such as polarized structure, desirable spectral properties, and high photoactivity. The outstanding photoreactivity has allowed coumarin to find wide photopolymerization applications. Coumarin derivatives are used as photosensitizers in cationic and radical polymerization.[1] However, coumarins are particularly important because they are perfect for one-component photoinitiating systems.

The use of the coumarin chromophore in the structure of iodonium salts was a breakthrough in the design of iodonium salts. Until then, one-component iodonium photoinitiators were simple diaryliodonium salts proposed in the 1970s by Prof. Crivello.[2] These salts have the significant disadvantage of poor absorption above 300 nm, which limits their applications. The new iodonium salts solve this problem with their efficient absorbing coumarin chromophore and the push-pull effect in their structure.[3]

The influence of the arrangement of electron-donating substituents in the coumarin chromophore on their photophysical properties and photoinitiating activity is analyzed. Five new coumarin-based iodonium salts exhibit two patterns of D–π-A structure – longer and shorter. They differ in the strength of the push–pull effect, which determines all properties of such compounds. Due to the intense ICT absorption band, new photoinitiators a reactive at 365 nm, 405 nm, and 415 nm. They exhibit excellent photoinitiating activity toward monomers such as vinyl ethers, epoxides, oxetanes, and glycidyl ethers at room temperature.[4] Coumarin-based iodonium salts proved to be excellent photoinitiators for nanocomposite DLP 3D-VAT printing.

Acknowledgments: The presented work was funded by the OPUS LAP project contract number 2020/39/I/ST5/03556 “Advanced photopolymerized nanocomposite materials processed by additive manufacturing”.

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Network analysis of a bond-percolation model of bi-functional monomers under photoirradiation and experimental validation

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Radical UV-curable resins are widely used in industry, and elucidating their curing mechanisms is essential for formulation and process design. Since cure shrinkage and residual stress, which are the fate of radical UV-curable resins, determine the long-term reliability of components, it is necessary from an engineering point of view to establish a method to predict them.

This study found experimentally that the shear modulus decreases with increasing irradiance when measurements are made at different UV intensities at the same UV exposure dose. We investigated what kind of network structure is responsible for this decrease in shear modulus. First, a simulation program was developed to construct a bond-percolation network structure based on Wen et al.'s study. Structural mechanical analysis was performed based on the developed network structure. The shear modulus for the network structure was compared with experimental results. The experimental and simulation results showed that the shear modulus decreased with increasing irradiance. The numerical values did not agree, but the order did. The network structure obtained from the simulation was studied in detail in terms of the contribution of each bond in the network to the elastic modulus. It was found that the web produced by increasing the irradiance had many sols formed in the early stages of the reaction. These sols were present after the reaction as dangling clusters. The elastic modulus decreases at high irradiance because these sols are present after the reaction as dangling clusters, which have a small contribution to the elastic modulus.

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Engineering Nanostructured Materials via 3D Printing and Polymerization Induced Microphase Separation

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Abstract: Currently, there are no straightforward methods to 3D print materials with nanoscale control over morphological and functional properties. In this talk, a novel approach for the fabrication of materials with controlled nanoscale morphologies using a rapid and commercially available Digital Light Processing 3D printing technique will be presented. The approach uses a controlled/living radical polymerization technique, more specifically, reversible addition-fragmentation chain-transfer (RAFT) polymerization, to control the topologies of the polymers.[1-2] In this talk, we report a rapid visible light mediated polymerization process and applied it to a 3D printing system.[3] Following the optimization of the resin formulation, a variety of 3D printing conditions will be presented to prepare functional materials.[4] The mechanical properties of these 3D printed materials were investigated under different conditions, showing that the control of the polymer structure can affect the performance of these materials.[5] Furthermore, the polymer networks were able to be reactivated after the initial 3D printing process, which allowed the post functionalization of the printed materials via secondary photopolymerization processes, enabling to introduce information.[6] Finally, by controlling the polymer architecture, we were able to precisely control the nanostructure of these 3D printed materials via a polymerization induced microphase separation.[7] The effect of nanostructure on 3D printed material properties will be discussed as well as their potential applications in drug delivery and energy storage, such as their use as solid polymer electrolytes for supercapacitor application.

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Design and synthesis of chalcone photoinitiator

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Chalcone derivatives possess significant potential as LED-sensitive photoinitiators (PIs) due to their affordability, facile synthesis, and ability to undergo photochemical hydrogen abstraction with tertiary amines. In this report, we present a comprehensive overview of our group's efforts in the development and commercialization of chalcone PIs.[1–4] Additionally, we propose unexpected properties of the designed chalcones, including solid-liquid transformation,[5] acidichromism,[6] and controllable activity[7,8] under irradiation, which hold potential implications for chalcones being applied in the field of photo-chemistry.

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New Generation of Oxime-ester Photoinitiators: Unveiling New Structures, Mechanisms, and Applications

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Oxime-ester photoinitiators are currently the most popularly used photoinitiators in color photoresists, which are critical for modern microelectronics industry. Therefore, to develop an efficient strategy to design highly photosensitive oxime-ester photoinitiators has been a hot research topic worldwide[1-2]. One promising method to enhance the photosensitivity of oxime-esters is to increase the quantum yield of the active free radicals. However, the traditional oxime-esters, after absorbing one photon, can produce only one active free radical because the generated iminyl radical is unable to initiate polymerization of acrylates. Therefore, the limiting value of the quantum yield of active free radicals is 1. We propose a new approach to boost the quantum yield of active free radicals based on photoinduced free radical transfer mechanism. With elaborate molecular design, the formed iminyl radicals with low initiation activity can be converted to alkyl radicals with strong initiation ability via intermolecular cyclization or ring-opening reactions. Therefore, the maximum quantum yield of the active free radicals could be raised from 1 to 2, effectively enhancing the initiating efficiency compared to conventional oxime-ester photoinitiators.

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Improved Cochlear Implant Biomaterials through Photopolymerization

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Cochlear implants (CIs) help restore basic auditory function in patients who are deaf or have profound hearing loss. CI electrode arrays are made of platinum wires and contacts encased in a silastic housing. These materials provide mechanical stability and flexibility critical to the long-term function of the CI. However, they also induce local tissue reactions that can have detrimental effects. For example, trauma from insertion of the CI can damage cochlear health and any residual acoustic hearing. Further, the fibrotic capsule that encases CI electrode arrays leads to increased impedances and decreased signal resolution which reduce CI effectiveness. Intracochlear fibrosis is also implicated in the loss of acoustic hearing that can occur months to years after implantation. Thus, developing materials that mitigate insertion trauma and the inflammatory, fibrous response to CI materials could significantly improve device function and safety. Ultra-low fouling zwitterionic polymers are a class of materials that show significant promise to reduce fibrosis. However as bulk materials they lack mechanical properties and long-term durability suitable for use in CIs.

To leverage the ultra-low fouling surface properties of zwitterionic polymers while maintaining the proven mechanical properties of current CI materials, we have developed a photochemical process for simultaneous polymerization, grafting and cross-linking of zwitterionic thin films on relevant CI materials. Photopolymerization has been used to covalently graft hydrogels of sulfobetaine methacrylate (SBMA) and carboxybetaine methacrylate (CBMA), two zwitterionic monomers, to PDMS surfaces. To produce the photografted hydrogels, the balance between crosslinker, photoinitiator and zwitterionic monomer is critical to impart sufficient mechanical stability and anti-fouling capacity. With a lower (5-30 wt%) range of crosslinker, films induce a greater than 90% decrease in cell and protein attachment. Incorporating appropriate amounts of crosslinker, zwitterionic monomer, and photoinitiator enables the hydrated coating to remain attached and viable under significant normal forces and bending. Failure due to bending or normal force only initiates after drying in ambient conditions for 60 minutes, demonstrating sufficient durability under typical handling conditions.

These zwitterionic coatings also produce a much more lubricious surface which leads to a reduction of up to 95% in the coefficient of friction relative to uncoated PDMS, thereby dramatically reducing the required insertion force for implantation. The effect of thin film photografted zwitterionic coatings on fibrosis reduction has also been demonstrated *in vivo* using model implants and human cochlear implant electrode arrays, exhibiting a fibrotic capsule thickness reduction of at least 50% regardless of surface geometry, duration of implant (up to one year), or the material coated. Additionally, coatings on CI arrays have shown up to a 50% decrease in impedance for systems implanted in sheep which demonstrates the potential of these photografted and photopolymerized materials in improving CI effectiveness. These results demonstrate that grafted zwitterionic thin films could lead to significantly reduced scarring and fibrosis for a variety of different biomaterials.

BIO-BASED MONOMERS AND RESINS FOR PHOTOCURABLE COATINGS

Mats Johansson

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The search for more sustainable materials solutions in society include several different aspects ranging from energy efficient processing techniques to the introduction of new raw materials with a lower carbon footprint. This can in field of coatings technology for example be the combination of UV-curing and new monomers derived from renewable resources. The bio-based monomers can either be retrieved directly from biomass (e.g. vegetable oils or terpenes), or be derived from renewable resources (e.g. itaconic acid, epoxidized vegetable oils, allylated lignin, etc.) [1]. Starting from biomass in some cases allows for totally new combinations of functionalities to be made. It is for example possible to retrieve monomers with both carboxylic acid, alcohol, and epoxy functionalities within the same molecule which would be difficult or tedious to make via conventional synthesis [2], [3], [4]. The use of these type of monomers in resin synthesis also in many cases involve new routes and processing techniques such as the use of sCO_2 as “solvents” [5].

The presentation will address how bio-based monomers and resins can be designed to give formulations with tailorable properties. The systems will be described with respect to curing kinetics, how these monomers homo- and copolymerize, and how the crosslinking chemistry can be adapted to specific functionalities of the resins. A main focus will be on free radical polymerization either using different alkene monomers or combinations thereof by themselves or combinations with different thiol-monomers to enhance the reactivity of the alkenes.

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PHOTOPOLYMERIZATION IN COVALENT ADAPTABLE NETWORKS

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Pursuit of materials to meet the needs of emerging technologies, however, has led to the development of polymers with pre-engineered, non-permanent linkages holding them together. Dynamic covalent chemistries (DCC), coupling reactions or functional groups that exhibit the ability of either reversible addition or reversible exchange, can be incorporated into polymers to provide the capability to respond to exogenous or endogenous signals.

When applied within crosslinked polymers, these materials (designated covalent adaptable networks or CANs) may adopt many of the advantages of thermoplastics (e.g. processability, recyclability) while maintaining those advantages of crosslinked polymers (e.g. high strength). User control over CANs extends further than that when DCCs are combined with other modes of responsiveness in materials such as shape memory or liquid crystal alignment, resulting in materials that change modulus, shape, size, color, etc. upon exposure to multiple selective stimuli, either sequentially or simultaneously.

Photopolymerization and photochemistry more generally have been employed in the creation and manipulation of CANs via several overlapping strategies. Photopolymerization provides a means for curing CANs. The Bowman group has used photomediated radical chain addition, thiol-ene, Michael addition, Huisgen cycloaddition, disulfide exchange and other reactions to generate CANs. Further, the DCCs themselves, and not only the polymerization, may be photomediated. The Bowman groups has used photolatent acids and bases to control base-catalyzed thiol-thioester exchange in networs and has used radical photoinitators to drive bond exchange in disulfides, allyl sulfide, and trithiocarbonate within CANs. Finally, the availability of photomediated reactions with varying mechanisms allows employment of DCCs in multistage polymerized materials capable of responding independently to multiple, orthogonal stimuli, enabling design and development of ever smarter smart materials.

The toolbox of photopolymerization and photomediated dynamic chemistries is extensive and expanding, indicative of broad interest in their research and applications. PhotoCANs hold potential to address needs in fields as diverse as optical devices to additive manufacturing to biomedicine through the development of materials capable of otherwise unachievable characteristics.

LATENT CATALYSTS IN DYNAMIC PHOTOPOLYMER NETWORKS

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Latent catalysts are a versatile approach to temporally and locally control the rate of bond exchange reactions and the related material flow in dynamic polymer networks. In particular, we explored novel families of photolatent transesterification catalysts to equip dynamic covalent networks with creep resistance as well as high bond exchange rate (once activated). The applicability of various (commercially available) photolatent acids was demonstrated by exploiting the orthogonality between the curing (410 nm) of a thiol-acrylate photopolymer and the activation reaction of the catalyst (365 nm).[1, 2] Recently, we applied photochemically (UV light) generated acids to catalyze a deprotection reaction of a tert-butoxycarbonyl group, which was employed to mask the hydroxy groups of a vinyl monomer.[3] At the same time, the released acid served as a catalyst for thermo-activated transesterifications between the deprotected hydroxyl and ester moieties in an orthogonally-cured (450 nm) thiol-click photopolymer. We further incorporated thermally stable photolatent bases (e.g. quaternary ammonium salts [4] and *N*-substituted derivatives of the amidine base 1,5-diazabicyclo[4.3.0]non-5-ene [5]) in thiol-click networks and realized a local and temporal change in material reflow due to the light-mediated release of strong Brønsted bases. In a follow-up study, we reported on the application of a photolatent transesterification catalyst, which releases a strong guanidine base upon irradiation with 405 nm LED light.[6] Incorporated in a visible-light-cured (450 nm) thiol-ene polymer, spatially resolved catalyst activation enabled a selective rearrangement of the network topology via thermo-activated transesterification. As the liberated catalyst (tetramethylguanidine) is volatile, the network was reverted back to a permanent one by a simple heat treatment at 210 °C for 10 min. We further studied thermolatent catalysts, whose activation is not limited by sample geometry and optical transparency of the materials. As proof of principle, the selective activation of dynamic transesterification was shown in fiber-reinforced and highly filled magneto-active thiol-ene polymer composites giving rise to the wide range of potential future applications offered by this concept.[7]

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On Demand Switching of Polymerization Mechanism

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Obtaining control over polymer chain growth in cationic polymerizations with an external stimulus would expand the utility of these methods and allow the synthesis of novel complex architectures. This presentation will detail the development of a cationic polymerization reactions regulated by visible light and electrochemistry. These polymerizations proceed under mild conditions and allow for the synthesis of various poly(vinyl ether)s with good control over molar mass and dispersity. Additionally, combining these methods with photocontrolled radical polymerizations enables switching of polymerization mechanism and, hence, monomer selectivity in situ to give control over polymer sequence and structure.

1.

LIGHT ON – CURING OFF: USING ORTHOGONAL PHOTOREACTIONS TO CHANGE CURING KINETICS IN THIOL-ENE SYSTEMS

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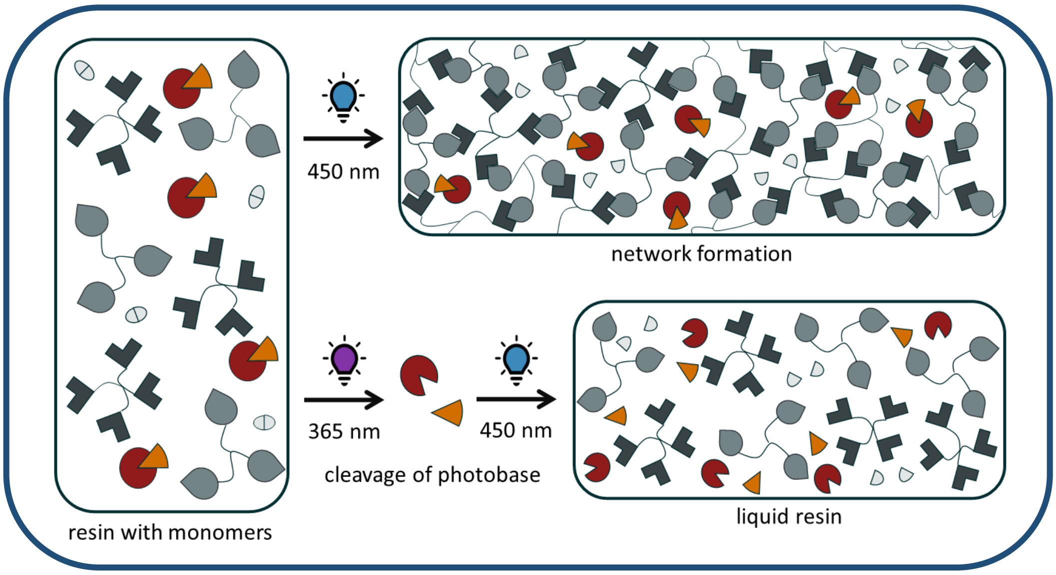
Thiol-ene chemistry has been a target of comprehensive research for several years, with a special focus on its use in photochemistry. Usually, thiol-ene free-radical reactions are a prominent example of click chemistry – showcasing high yields, a variety of possible monomers and orthogonality towards most other reactions employing functional groups – to name a few characteristics [1]. Especially in 3D-printing for medical applications, otherwise commonly used acrylates are replaced by thiol-ene based resins due to their better biocompatibility.

As previously introduced by Bowman et al., basic amines retard the thiol-ene reaction under certain conditions – mostly dependent on the pKa of the thiol in comparison to the amines' conjugated acids pKa [2]. We transferred this concept to photochemically activated basic compounds to gain additional control over the thiol-ene curing reaction. In our resin system radical curing is activated through a Type II photoinitiator which is most active at 450 nm, whilst having a minimum in absorptivity at 365 nm. Therefore, light with a wavelength of 365 nm is used to trigger the activation of the photolatent base, resulting in an inhibition of the curing reaction. By adapting the amount of photolatent base and the illumination time with 365 nm, it is possible to gain control of the curing kinetics through the use of light. Controlled inhibition and retardation of the thiol-ene curing reaction open the doors to numerous possibilities, such as applications in 3D-printing or advanced photolithography.



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Cooperative Network Formation via Two-Colour Light-Activated λ-Orthogonal Chromophores

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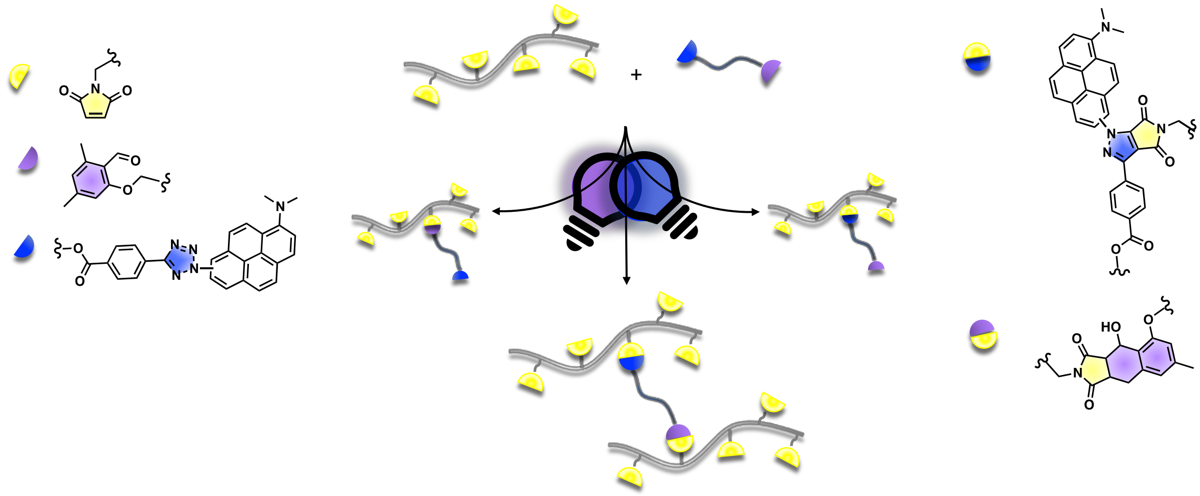
Propelling a specific reaction independently by activating only one of the photoreactive sites within a single molecule is a formidable challenge. Here, a heterotelechelic dilinker molecule is synthesized by combining two fully sequence-independent λ-orthogonal chromophores to exploit their disparate reactivity with the same reaction partner, a maleimide-containing polymer. It is shown that the network formation only occurs when the system is exposed to irradiation with two colours of light either in a sequence-independent stepwise or in a simultaneous fashion. One-colour irradiation activates solely one of the photoreactive sites, resulting in a linker-decorated post-functionalized polymer. The functionalized polymers formed after each separate irradiation with one color of light was characterized using ^{1}H-NMR spectroscopy. The changes in the topology of the maleimide decorated polymer after each irradiation step and onset of crosslinking upon two-colour irradiation were monitored by size exclusion chromatography. Finally, physical gelation was observed solely upon exposure of the resin to two colours of light, but not upon exposure to one colour. The newly introduced photoreactive system reveals the potential of wavelength orthogonal chemistry in precision macromolecular synthesis.



Scheme 1. Illustration depicting the photochemical polymer post-functionalization with one colour of light irradiation and cooperative network formation with two colours of light irradiation of the photoreactive system comprising a maleimide-containing polymer and a heterotelechelic dilinker with UV (325 nm) and/or blue (450 nm) LEDs.

On the Cleavage of Alkoxyamines: Prospects of "Smart" Mediation Systems for Radical Polymerization Reactions

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Alkoxyamines have attracted scientific interest due to their ability to decompose into radicals under mild and controllable conditions. The involved fragmentation pathways can however be complex and are highly dependent on the reaction conditions. While oxidation of the parent alkoxyamine yields radicals by mesolysis of a radical cation intermediate[1], photochemical and thermal decomposition proceeds directly via C-O homolysis[2]. Proton transfer reactions on substituents may introduce further fragmentation pathways. Decomposition however often yields nitroxide radicals. If released in a controlled and selective way, they can serve as "smart" mediators for radical polymerization reactions. For such applications, it is crucial to get a holistic view on alkoxyamine reactivity.

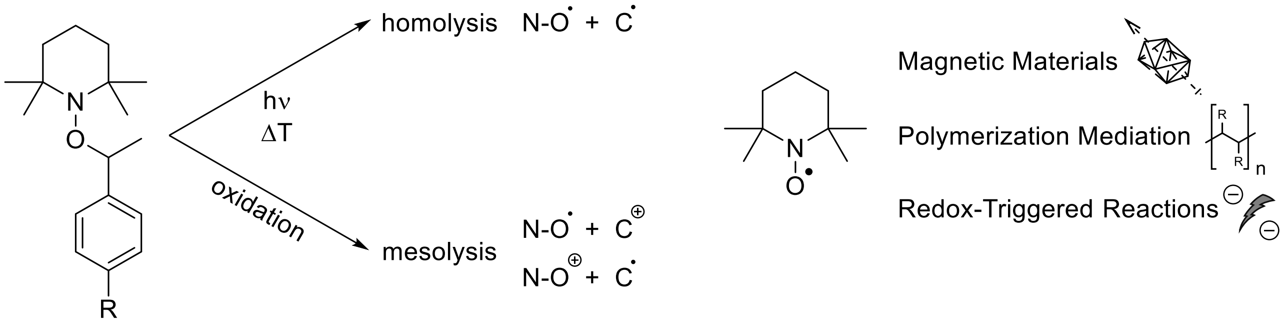

Figure 1: General decomposition pathways of an alkoxyamine (left) and possible applications of released nitroxide radicals (right).

Following a mechanistic approach, we will elaborate on the reactivity of selected alkoxyamines and the influence of substituents on their cleavage pathways. In doing so, we will illustrate how synergistically employing theoretical, electrochemical and spectroscopic (EPR/CIDNP) methods can shine light on the underlying fragmentation processes.

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Red-light induced emulsion photopolymerization

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Photopolymerization is a light induced process offering significant advantages compared to thermal process in terms of safety, mainly due to their low energy consumption, use of low temperature and reduced emissions of volatile organic compounds (VOCs).[1] This process will be more favorable when using an economical, safer light source with deeper light penetration such as red light (620-780nm), which is more advantageous than others at shorter wavelengths.[2] On the other hand, emulsion polymerization is a process for producing fluid latex in an aqueous suspension, i.e. in an affordable, safe and green solvent, with a particle size between 50 and 500 nm. It occupies an important place in many industrial sectors, such as coatings, adhesives, paints, additives for constructions materials and non-woven textiles.[3] Therefore, it is interesting to combine the advantages of both processes. Then, emulsion photopolymerization requires a water-soluble, red-light sensitive photinitiating system (PIS). In this context, methylene blue (MB) was used as red-absorbing photoinitiator (PI), combined with a co-initiator (coI) such as sodium para-toluene sulfinate (NapTS), for the photopolymerization of methyl methacrylate (MMA). In this work, poly(methylmethacrylate) (PMMA) latexes were synthetized following irradiation with a LED @ 660 nm. These latexes were characterized using different technics, polymerization kinetics were determined by gravimetry and their photoinitiating mechanisms were investigated through a variety of methods, including fluorescence spectroscopy, steady state photolysis and light transmission measurements (experimental and simulated).

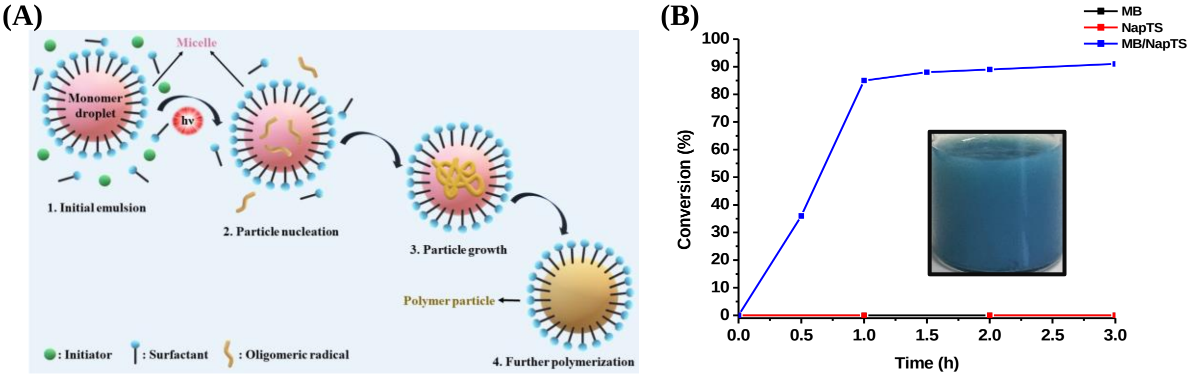

Figure: (A) Emulsion photopolymerization mechanism; (B) Photopolymerization profile of PMMA latex.

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FRONTAL POLYMERIZATION AS ENERGY-EFFICIENT WAY TOWARDS COMPOSITES

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Radical Induced Cationic Frontal Polymerization (RICFP) is a cationic ring-opening polymerization applicable for different industrially relevant resins like epoxides, oxetanes or vinyl ethers. In this process, an initial and locally limited stimulus starts the polymerization reaction, which in turn triggers a self-sustaining and propagating curing “wave” throughout the whole resin. As only this first energy input is needed, this makes it a faster and more energy-efficient curing method than the state of the art methods for curing such resins, which often include long curing cycles using autoclaves.

The principle is already well-established in academia, with literature showing its use in pure resin systems[1,2], particle and fiber filled composites[3] as well as prepregs.[4] Especially with the recent advances in this field, different industries have shown interest in frontal polymerization as it could become a useful out-of-autoclave solution for composites.

Herein, radical induced cationic frontal polymerization will be presented with all of its advantages and disadvantages, as well as adaptations of the process towards industry. Overall, the progress from unfilled systems towards composites and the application in filament winding of tanks will be covered.

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PRODUCTION OF PHU COATING AND FOAMS VIA NEAR-INFRA-RED IRRADIATION

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Polyhydroxyurethane (PHU), obtained from the reaction of cyclocarbonates and amines, represent an eco-friendly alternative to conventionnal polyurethanes because their synthesis relies on CO2-based precursors and does not involve toxic isocyanates compounds. However, the low reactivity of the cyclocarbonate aminolysis to form PHU represents a major drawback, particularly for industrialisation[1]. Although the reaction can be accelerated in the presence of catalyst or by heating using oven there is still a gap of reactivity between isocyanate-alcohol and cyclocarbonate-amine additions. To overcome the lack of reactivity between cyclocarbonates and amines, we thus propose to use the photothermal effect generated by some compounds absorbing in the Near-Infra-Red (NIR) region. Indeed, photothermal effect, which consists in the production of heat at local environment by some metallic nanoparticles or organic dyes under NIR radiation, has proven very effective for increasing reaction kinetics, particularly for the synthesis of PU thermoset[2]. As NIR sensitive compound we chose the organic dye IR-813 (Figure 1) because of its commercial availability and its good solubility in organic resins. It was added to a formulation composed of trimethylolpropane tricarbonate (TMPTC) and 1,5-pentanediamine and curing of the formulation under NIR light (805 nm) was then studied. Various parameters were varied such as the amount of heater or intensity of irradiation and their influence on gel time and maximum temperature reached were evaluated. Then, the best system was used for the production of PHU coatings and foams.

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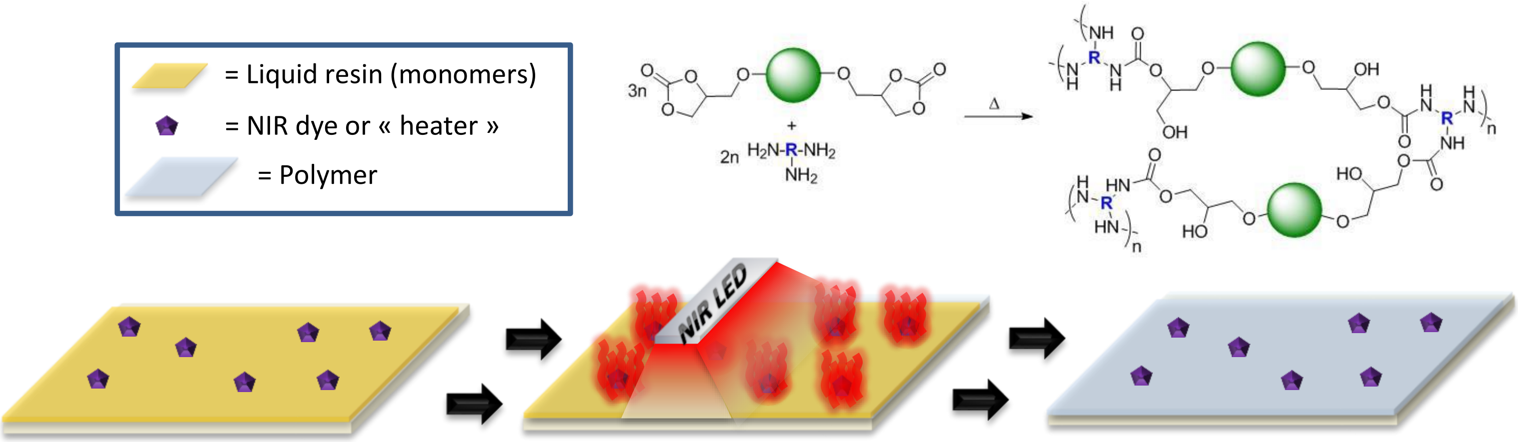

Photoactive Polymeric Dormants: New Design of Functional Coatings with Nanostructured Domains via "Controlled" UV-Curing Process

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UV-curing process based on photo-induced radical polymerization has been widely utilized for inks, paints, adhesives, and photo-resist materials. Especially, facile tuning of UV intensity, wavelength, irradiation area etc, has enabled their industrial applications, however the precise control of photo-polymerization is not trivial due to their too rapid reaction time (within seconds). Delicate balance of reaction kinetics, deformation (shrinkage), and phase-separation associated to polymer network formation needs to be considered.

Reversible deactivation radical polymerization (RDRP) techniques such as atom-transfer controlled radical polymerization (ATRP) have greatly impacted the advancement of polymer synthesis in the last 20 years, allowing well-defined polymers with precise molecular weight distribution and segment blocks. Recently, further temporal (on/off) control of polymerization via external stimuli such as photo-excitation has proposed and gained increased attention. We have focused on organo-catalyzed iodine-mediated controlled radical polymerization and developed photoactive polymeric dormant with C-I endgroup. The polymeric dormant was utilized to the UV-curing process to give optically clear coatings with unique bicontinuous morphology with gradient size distribution. The nanodomains were evolved via polymerization-induced microphase separation (PIMS), and kinetically trapped by crosslinking. Here we design functional polymeric dormant to selectively functionalize the evolved nanodomains. Surface wettability and optical properties, etc was tunable with functional nanodomains. Hierarchical nanostructures with macro-/microphase-separated domains were also developed by our method, and potential applications will be also discussed.

MONITORING PHYSICAL TRANSFORMATIONS ON THE NANOSCALE IN REAL-TIME DURING PHOTO-INITIATED POLYMER NETWORK FORMATION USING X-RAY SCATTERING

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Elucidating nanostructure-property relations is vital for tailoring macroscale properties of functional materials. Hereby, it is essential to observe physical transformations in situ and in real-time during the materials´ processing. Such physical transformations are induced by external stimuli, for example temperature [1] or UV-light in case of photopolymerization [2]. Excellently suited for this task are scattering methods using X-rays and neutrons when applied as analytical methods. Owing to their ability to penetrate into material, complex processing environments mimicking real-world, industrially relevant conditions are incorporated in such investigations. In order to show the tremendous potential of this combination, we will highlight various examples. To start with, we use a model system of polystyrene colloids with chemically different shell to describe the heat-induced morphological changes in such latex films [3]. The kinetics of layer formation and the final nanostructure, e.g. in additive manufacturing, strongly depend on the processing conditions [4]. Towing polymer processing, we elucidate the fundamentals of injection moulding [5], all in combination with scattering methods. Using these examples as basis, we highlight the use of surface-sensitive X-ray scattering to investigate the evolution of heterogeneities in UV-curable resins [6]. We detail the influence of glass transition temperature on the physical transformation during UV curing and relate the final film morphology to the molecular structure. We give an outlook how these advanced analytical techniques will be extended to 3D printing using photopolymerization.

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Waves of Photopolymerisation, Frontal Instabilities and Novel 3D Patterning Routes

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Patterning of soft matter provides exceptional routes for the generation of micro/nanostructured and functional surfaces, for controlled adhesion, wetting, spreading and fouling, drag reduction or anti-microbial properties. We describe the propagation of planar wavefronts of network formation emanating from an illuminated surface during photopolymerisation and report a 3D patterning approach based on coupling planar growth with precisely controlled, yet spontaneous, interfacial instabilities. Photopolymerisation is a complex spatio-temporal process that may lead to well-defined solidification fronts, both stable and unstable. We investigate this light-driven frontal photopolymerisation (FPP) process with a combination of experiments, analytical and numerical modelling. Frontal growth of a series of multifunctional radical monomers can be quantified and described with coarse-grained models characterising the extent of monomer-to-polymer conversion [1-3]. The non-trivial aspects of FPP derive from the coupling of optical attenuation coefficient and the growing non-uniform network, and can be readily modulated by chemical formulation and light processing, as well as by the effects of temperature. Using these results, FPP is demonstrated as a photolithographic 3D fabrication process [4], avoiding multiple illumination steps.

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ESPERANTO
Enhancing the Sustainability of PhotopolymERs ANd phoToinduced prOcesses

Funded by the European Union

PHOTO-THERMAL DUAL CURED BLENDS OF TiO_2/DIARYLFLUORENE FILMS WITH HIGH REFRACTIVE INDICES

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Organic-inorganic hybrid nanocomposite materials have attracted much attention to improve physical and chemical properties of organic materials[1]. In this point of view, Matsukawa et al. reported the preparation of organic-inorganic hybrid films having high refractive indices[2-4]. They used TiO_2 and ZnO_2 as inorganic compounds, which gave high refractive indices. We also reported the fabrication of photocured films of diphenyl- or dinaphthylfluorene having acryl, epoxy, and oxetane moieties and polysilanes blends[5-8]. We have successfully fabricated the films with high refractive indices (n_D: 1.62) and the decrease of about a 0.03 refractive index was observed after the photodecomposition at 254 nm with a dose of 18000 mJ/cm^2 [7]. The prepared films have a high thermal stability (temperature for 5% weight loss, T_{d5}: 300 ºC) [7].

In this study, we employed TiO_2 nanoparticle as an inorganic compound. We developed the photocured films of a blend of TiO_2 nanoparticles and dinaphthylfluorene derivatives having acryl and thiol groups and a photoinitiator by photo-thermal dual curing technique. The optical and thermal properties of the photocured films were investigated. The photocuring mechanism was also discussed. The curing properties of the blends were strongly affected by the photo-thermal dual curing conditions. We successfully fabricated films with high refractive indices (1.693 at 589 nm) and high thermal stability (5% weight loss temperature: 266 ºC).

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ADVANCED POLYMERIZATION TECHNIQUES IN SURFACE ENGINEERING.

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The development of reversible deactivation radical polymerization (RDRP) methods, such as atom transfer radical polymerization (ATRP), has enabled the creation of densely packed polymer brushes by offering precise control over polymer chain length, distribution, and structural characteristics. Leveraging these attributes and combining with a wide variety of functional monomers allows us to impart desired properties, including hydrophobic or hydrophilic characteristics, bio-resistant or bioactive features, stimuli-responsive behaviour, low-friction attributes, anti-corrosiveness, etc [1]. Photoinduced atom transfer radical polymerization (photo-ATRP) offers several advantages compared to other ATRP methods due to its cost-effectiveness, improved tolerance towards oxygen, milder reaction conditions, and the ability to achieve temporal control over polymerization without the need for additional chemicals [2, 3]. These characteristics of photoATRP in surface modification via surfaces-initiated photoATRP make it an invaluable tool for the synthesis of well-controlled polymer brushes over large areas, using minimal reaction volumes [4].

This work presents the synthesis of highly dense and uniform poly(α-methylene-γ-butyrolactone) (PMBL) brushes on Si-wafers. Utilizing custom-made polymerization setups ensured a high level of uniformity across the substrate, even at the edges. Notably, one of our setups facilitates PMBL brush growth in open air, a novel finding. Synthesis was successfully replicated under natural sunlight and in complete darkness after brief UV exposure, offering potential economic benefits. Moreover, the reaction mixture proved reusable for up to two cycles, resulting in PMBL brushes exceeding 40 nm in thickness. Encouraged by these findings, we extended the process to include modification of other surface oxide layers.

Acknowledgment

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CO2-derived non-isocyanate polyurethane based self-etching dental adhesive system

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Denal adhesives play the main role in the restoration process by making an appropriate bonded interface between tooth cavity and dental composites. So, the development of dental adhesives has considerably affected the clinical applications and efficiency of the dental composites. Self-etching adhesives are generally a mixture of components with acidic functional groups that can diffuse between the collagen fibrils to form micro-retentive resin tags and create the hybrid layer. Here, we reported a new self- etching dental adhesive based on non-isocyanate urethane linkages. The urethane linkages have better hydrolytic stability and also can enhance intermolecular interaction. Hence, we functionalized epoxy monomers with CO_2 (as an abundant and inexpensive carbon feedstock) to synthesis the key building block cyclic carbonates. Then through the interaction with amine components we synthesized the monomers/oligomers containing non-isocyanate urethane linkages and acidic moieties. The new self- etching dental adhesive can show appropriate hydrolytic stability and bonding properties.

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Photoinduced surface initiated ATRP:

Towards microfabrications by Control Radical Polymerizations.

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In the early 20th century, the Italian physico-chemist, Giacomo Luigi Ciamician, highlighted the interest of using light as a suitable energy source for chemical reactions.

At the end of this same century, polymer chemistry had a breakthrough thanks to the discovery of Control Radical Polymerizations (CRP) allowing to regulate molecular mass, polydispersity, chain end… In particular, Atom Transfer Radical Polymerization (ATRP) was independently developed by Krzysztof Matyjaszewski and Mitsuo Sawamoto in 1995. One of the applications of this polymer growth mechanism is surface functionalization, also called surface-initiated ATRP (SI-ATRP), with brush polymer structure and with possible chain-end modifications.

Thus, this talk will present our ongoing works on the development of a new system for photoinduced ATRP of bio-oriented monomers obtaining functionalized polymers. In particular, we will discuss the possibility of inducing photo-mediated SI-ATRP by one or non-linear two photon mechanism or by Low One Photon Absorption (LOPA). This could allow getting high resolution 3D stereolithography, surface coating and functionalization.

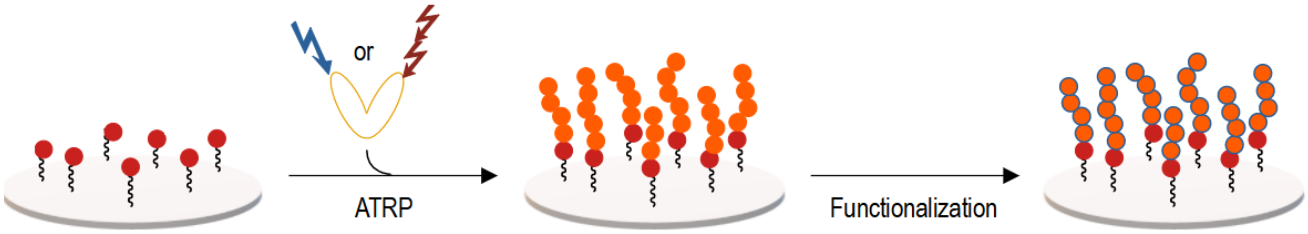

Figure 1 - Surface functionalization by photoinduced Surface Initiated ATRP.

PHOTO-CURABLE THIOL-ENE / NANOCELLULOSE ELASTOMERIC COMPOSITES FOR BIO-INSPIRED AND FLUORINE-FREE SUPERHYDROPHOBIC SURFACES

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Cellulose nanofibrils are attractive candidate biomaterials for polymer composites owing to their superior characteristics compared to organic resins such as biocompatibility, biodegradability, process-induced anisotropy of the composite due to high aspect ratio, tunable surface chemistry and reinforcement capability; however, the widespread utilization of these biobased materials remains limited, especially for applications involving photopolymerization [1]. In this work, a photo-curable thiol-ene resin containing controlled concentrations of cellulose nanofibrils oxidized by 2,2,6,6-tetramethylpiperidine-N-oxyl (TEMPO) mediation (TOCNF) is prepared without dispersants or surfactants owing to surface modifications such as counter cation exchange of carboxyl and grafting of thiol and ene functional moieties. The rheological and photo-crosslinking behavior of the TOCNF suspensions, the thermal stability and the mechanical performance of the cured composite materials, and the hydrophobicity of lotus-replicated hierarchical surfaces are characterized [2]. The composite suspensions are shear thinning with power law exponents around 0.3 and their photo-conversion profiles significantly vary based on the grafted surface functionality with thiol modifiers causing a lower curing rate than enes. The cured composites show improved thermal resistance at elevated degradation temperatures above ~ 360°C, and outperform the neat thiol-ene polymer in terms of hardness (x5.8) and reduced modulus (x3.4). Moreover, the surface of composites texturized with a lotus leaf pattern is superhydrophobic with a water contact angle of 155°, higher than that of the neat and texturized polymer (147°). This was achieved without any surface treatment such as fluorination [3]. These results are useful to obtain mechanically and thermally robust photo-curable elastomers as well as to explore the potential of such composite resins in manufacturing processes requiring rapid curing such as 3D printing and roll-to-roll processing.

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Surface-functionalization with novel Germanium-based photoinitiators for surface-mediated, radical and cationic photopolymerization techniques

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During the last decades surface modification based on “grafting from” techniques have received an increasing interest in the industrial as well as in the academic sector. This approach relies on covalently coupled initiating species, that can be triggered either by heat or light, and subsequent (photo)polymerization reactions of functional monomers, which results in a surface-tethered polymer brush system. Typically, those (photo)initiators are coupled to inorganic surfaces via trialkoxysilyl, thiol or diazonium salt anchoring units. In the present work, a novel and visible light sensitive photoinitiator, based on germanium, was prepared and equipped with a halogen coupling unit. This compound was subsequently covalently coupled to spherically shaped SiO_2 nanoparticles and flat substrates. The generated light sensitive surfaces were then employed for surface-initiated free radical photopolymerization of different acrylates and vinyl monomers [1]. Furthermore, and for the first time, we report on surface-mediated cationic photopolymerization [2], also triggered by visible light (450 nm), using the same modified nanoparticles. In that manner, living polymer brushes, derived from vinyl ethers and epoxides were achieved. The surface composition as well as the grafting density were studied using, e.g., TGA, REM, FT-IR and XPS spectroscopy.

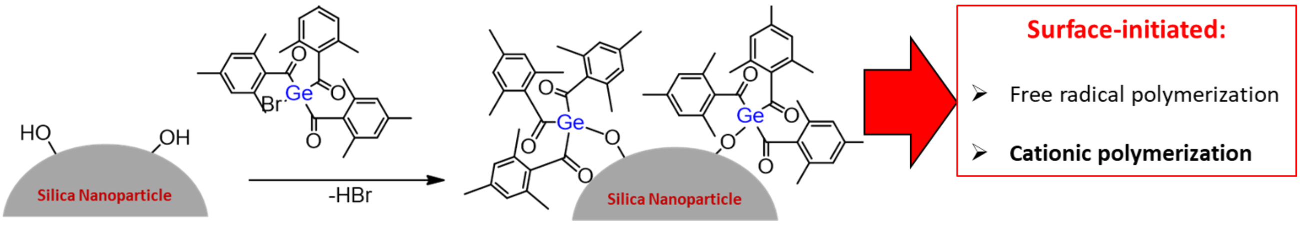

Fig. 1: Photoinitiator immobilization and subsequent grafting-from polymerization

Considering the outstanding advantages of this new and efficient class of photoinitiators, namely the high absorbance in the visible range of the spectrum (up to 485 nm) and low-toxicity, we believe that this technology has a high potential to open up high-end applications, especially in biomedicine.

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PHOTOPOLYMERS WITH ENHANCED THERMOMECHANICAL PROPERTIES FOR 3D PRINTING APPLICATIONS

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Digital light processing (DLP) is one of the most popular 3D printing techniques utilizing a light source for solidifying a liquid resin. High reactivity, limited resolution and thermomechanical properties are still the main obstacles to overcome. Acrylate resins are widely implemented in 3D printing. Despite their important reactivity and commercial availability, they suffer from yielding inhomogeneous and uncontrolled polymer structure and high crosslink density or limited mechanical properties. Different routes have been reported in the literature to tackle these drawbacks. This paper will highlight the potential of the aza-Michael addition or the incorporation of a reversible addition-fragmentation chain transfer (RAFT) agents or to control the polymer network structure and enhance the thermomechanical properties as elongation at break, toughness or SMP properties. In addition, the in- situ generation of an inorganic silicate phase will be discussed as an attractive route for hybrid organic-inorganic materials avoiding multi-step procedure and possible phase separation.

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Thioxanthone Dioxides: Synthesis, Photophysical and Photochemical Characterization

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Photoinitiators are critical components of photopolymerization formulations, allowing for effective initiation, control over curing kinetics, compatibility with multiple systems, adaptability, energy efficiency, and spatial/temporal control. Their importance stems from their capacity to accelerate the creation of sophisticated materials and enable novel applications in industries such as adhesives, coatings, electronics, 3D printing, and biomedical engineering.

Bond cleavage (type I) and H-abstraction type (type II) initiators can be used for photoinitiated radical polymerization. Thioxanthone (TX) and derivatives are among the most widely used Type II photoinitiators in various UV curing applications because of their excellent light absorption characteristics. In most cases, the polymerization-initiating free radicals are generated by hydrogen abstraction of the triplet excited state of TX from hydrogen donors such as amines or thiols.

The oxidized derivatives of TX, thioxanthen-9-one-10,10-dioxide derivatives, show biological activities including anti-tumor, anti-allergic, and monoamine oxidase (MAO) inhibitory activity and a wide range of pharmacological properties. However, only few studies of their photophysics and photochemistry have been published. Here we report the photochemical and photophysical properties of a series of TX-Dioxide derivatives and their use as photoinitiators for polymerization and in-situ prepared gold /silver nanoparticles in polymer matrix [1,2].

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WHICH WAYS FOR IMPROVING THE REACTIVITY OF PHOTOINITIATING SYSTEMS?

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Conventional Type I and Type II photoinitiators are used in photopolymerization area since more than 30 years. However, these systems faced two different problems: 1/ Type I photoinitiators are reaching a maximum of reactivity with compounds such as phosphine oxide and Type II photoiniators suffers from the decreased reactivity induced by the need of diffusion process.

In this paper, we investigate different ways to increase the reactivity of Type I or Type II photoinitiators by introducing latent reactive additives [1-], promoting photosensitization [2], pre-associating ion-pairs [3], … It is shown that high photopolymerization rates can be achieved even at very low light irradiances.

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PHOTOLATENT BASES PROVIDING OPPORTUNITIES BEYOND SIMPLE CURING

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Upon irradiation, photolatent bases release a strong amine base. The latter is a stable compound that is capable to catalyze crosslinking reactions, but also other types of base catalyzed transformations. Thus, a photolatent base is not a photoinitiator, but a photolatent catalyst.

Several classes of photolatent bases have been reported in the literature. Most examples are ionic compounds with a correspondingly limited solubility in organic formulations. In addition, ammonium carboxylate salts, widespread used as photolatent bases cause, due to an equilibrium with the non-caged amine catalyst, an inacceptable short shelf life of the formulations. Recently we have developed a novel photolatent amine being a non-ionic neutral organic compound with excellent solubility in organic formulations. Upon irradiation, the superbase 1,5-Diazabicyclo[4.3.0]non-5-en (DBN) is released.

Crosslinking reactions catalyzed by strong bases are inherently slower than those based on radically curing formulations. For some applications, this can be turned into an advantage, since it provides, after irradiation, a time window during which additional processing steps can be performed before full cure is achieved.[1]

Since the strong base released is a stable organic compound that, acting as a catalyst, is not consumed during the curing reaction,it remains reactive even in the absence of light, therefore allowing for full cure also in not fully irradiated regions. In addition to the crosslinking process, it can also concomitantly catalyze other transformations, such as the sol-gel reaction of siloxanes producing *in situ* siloxane nanoparticles, or the reduction of graphene oxide to graphene,[2] thereby generating organic-inorganic hybrid materials[3] [4] with outstanding properties. A further application is the formation of vitrimers.[5] In this case the latent form is used as catalyst for the thermal crosslinking of the organic matrix, while the strong amine formed upon irradiation is an excellent catalyst for transesterification reactions that provide spatio-temporal-controlled vitrimeric properties.

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THE FUTURE OF PHOTOINITIATORS IN THE 21TH CENTURY

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Currently there are many concerns regarding the toxicity and mutagenicity of certain very frequently used photoinitiators. Some benzophenones and acylphosphine oxides, to name only a few, a currently more or the less banned from the market and there is a huge hunt to find good substitutes.

Very recently, we have shown that aliphatic a-keto esters could be a good substitute, however limited reactivity and oxygen inhibition avoided broader use. Now we have identified so called “Crowded photoinitiators”, as a suitable alternative, that are able to compete with classical Type I initiators.

Long wavelength absorption is frequently also highly important, especially when it comes to pigmented formulations or for composites like in the dental field. Acyl tin compounds are highly interesting due to their long wavelength absorption and also surprisingly low toxicity but suffer from poor storage stability. Having the right substitution pattern allows now not only an absorption well beyond 550 nm, but also excellent storage stability, high reactivity, perfect photo-bleaching at an reasonable price.

While radical and cationic photoinitiators can be frequently found in industry, latent photo-bases suffer from a sleeping beauty sleep. Besides that, thiol ene photopolymerization is gaining more and more interest, thanks to the pioneering work of Hoyle and Bowman. While outstanding mechanical properties are a huge benefit, the sometimes bad odour and poor storage stability are an issue. The question is if alcohols are able to substitute those thiols. The answer is yes, with the right photo-latent base.

DEVELOPMENT OF UV-LED CURABLE BLACK INKS

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Keywords: photopolymerization, UV-LED curing, inks

Abstract: Today, transition to a low carbon footprint economy is driving automotive industry to drastically reduce their energy consumption and VOC emissions. Particularly, painting stage is responsible for up to 90% of emissions and 60% of energy consumption of an industrial automotive plant[1,2]. In this context, UV-LED curable inks combined with printing techniques offer a promising solution[3,4,5]. However, development of new printable formulations capable of combining environmental requirements with demanding automotive coatings specifications, REACH restrictions and process requirements like finish quality and surface complexity has proven to be a major challenge. As a result, we have developed 100% solids and UVA curable black inks, with viscosity of around 7 mPa.s. These systems are cured exclusively by radical photopolymerization, without using conventional photoinitiator systems for black inks, which are composed by REACH banned molecules. In addition, according to preliminary tests, their glass transition temperatures are higher than 80°C, which suggests they are suitable for automotive coatings applications in terms of mechanical properties.

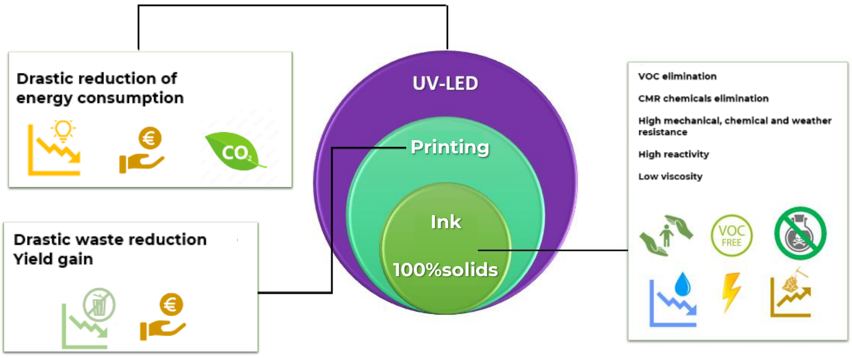

Figure 01: Curable inks advantages in the context of printing processes and UV-LED drying

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NOVEL LIGHT-RESPONSIVE BIO-BASED FOAMS IMPREGNATED WITH PHOTOREVERSIBLE PRECURSORS THROUGH PHOTO-INDUCED POLYMERIZATION FOR ON-DEMAND RESHAPING CAPABILITY

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This study presents the development of novel light-responsive bio-based foams with controllable compliance and shape, achieved with the utilization of photoreversible precursors. Effective incorporation of the photoreactive precursors into the open-cell foam is reached through the implementation of a liquid impregnation process [1]. The optical properties of the impregnated foam are modelled using scattering theory. The controlled crosslinking relies on the reversible nature of $[4\pi s + 4\pi s]$ or $[2\pi s + 2\pi s]$ cycloaddition reactions [2], creating an interpenetrating phase composite [3]. The research places a particular emphasis on the analysis of the photoreversibility degree exhibited by the cured composite foam. The cleavage of the photodimers is triggered by short wavelengths UV irradiation or by thermally induced bond scission. This property serves as a pivotal parameter for fine-tuning foam compliance through controlled partial depolymerization, subsequently followed by repolymerization. Moreover, a comprehensive life-cycle costing and assessment is undertaken to evaluate the economic feasibility and sustainability of implementing these advanced materials in practical applications.

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FRONTAL POLYMERIZATION OF DYNAMIC NETWORKS

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Frontal polymerization (FP) enables the conversion of monomers into polymers in a spatially confined reaction zone (front). There, the reaction zone spreads through the bulk material in an autocatalytic self-propagation, which is similar to an avalanche (Figure 1). The front is driven by exothermic heat generation, with the only necessary external energy input occurring during the initiation process. Frontal polymerization has been investigated for several monomers due to its rapid curing and its high energy efficiency. Of high relevance are epoxy resins, which are industrially abundant, as well as acrylate monomers. These are usually cured by photopolymerization or thermal processes.

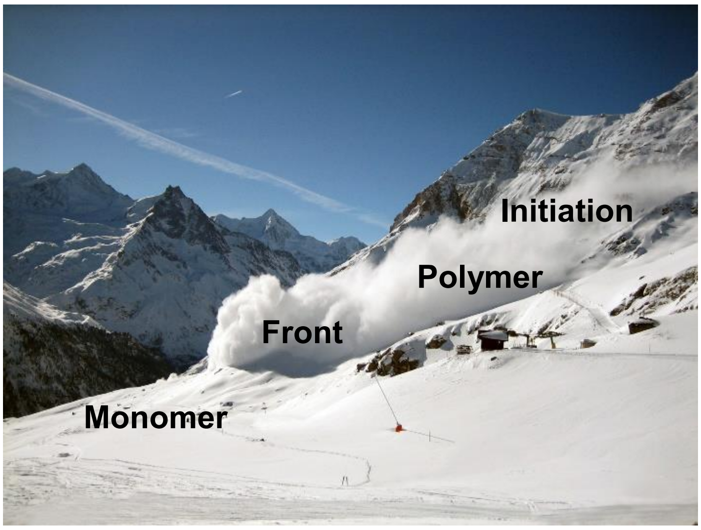

Figure 1_Frontal polymerization avalanche

However, both conventional thermal curing and photopolymerization suffer from serious disadvantages. In thermal polymerization processes, extensive curing times and high energy input are still issues, whereas photopolymerization is more rapid. Due to the low penetration depth of the light, only thin layers can be cured, though. To overcome these drawbacks, various kinds of frontal polymerization were employed. Similar to conventional thermally and photo-cured networks, the polymer networks formed are characterized by high chemical and thermomechanical resistance. Nowadays, other factors besides energy efficiency play an important role, such as recyclability, reusability and reprocessability. These can be implemented by the introduction of dynamic bonds into thermoset materials. Commonly, transesterification reactions between free hydroxy- and ester moieties are implemented by using suitable catalysts. In this work, various different types of dynamic bond exchange reactions have been investigated for their applicability in frontal polymerization.

Photoresponsive Molecules as Potential Candidates for Light-Induced Reversible Polymerization of Biobased Monomers

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As the world shifts towards greener economy, there is a demand to use less energy intensive processes for creating innovative materials[**1**]. And in bottom-up approaches to answer this call, molecules that undergo geometric and/or electronic changes through photon absorption instead of heat treatment are being explored. These molecules can be used in building self-healable and recyclable polymers through different photomediated reactions. Comprehensive library research had been conducted to better understand the advantages and disadvantages of their different mechanisms following three different perspectives – molecular, structural, and practical points of view.

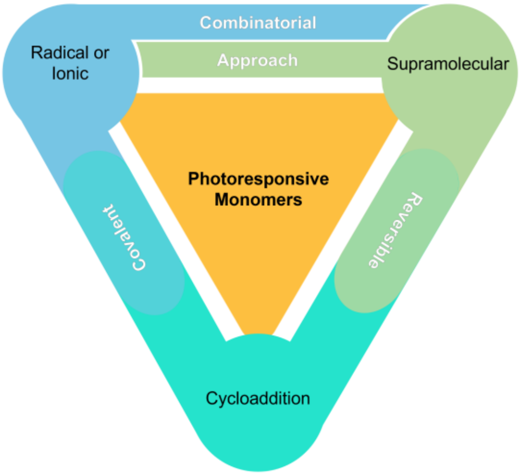

Figure 1. Interconnectedness of photomediated reactions *vis a vis* polymerization.

Early experimental works concerning the synthesis of new biobased monomers and their characterization had been carried out. To illustrate, coumarin-containing monomers were (co)-polymerized to investigate the extent of photocycloaddition. Introduction of conjunctive sources of energy (*i.e.* mechanical, electrochemical, thermal) was also tested to check whether this can improve the efficiency of decrosslinking. In the end, the aim is to provide a general framework in choosing suitable task-specific photoresponsive molecules in the context of sustainable formation of biobased composites[**2**].

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ESPERANTO
Enhancing the Sustainability of PhotopolymERs ANd phoToinduced prOcesses

Funded by the European Union

Surface-modification of Silica Nanoparticles with Germanium-based Photoinitiators and Subsequent Surface-mediated Cationic Polymerizations

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Nanoparticle's exceptionally high surface area and surface chemistry enable it to reach higher levels than other common drug delivery carriers. Surface modification based on “grafting from” techniques provided a versatile tool for industry. A novel and non-toxic, germanium-based photoinitiator[1] immobilised on the surface of silicon-based materials has been developed. Subsequent visible-light (405 nm) induced surface-initiated radical photopolymerization had remarkable efficiency and value. Herein, we report a combination of germanium-based photoinitiator immobilized on nanoparticles (20 nm and 200 nm) and diphenyliodonium hexafluorophosphate[2] which can initiate cationic polymerization under visible-light (450 nm). Employing visible-light-triggered surface-initiated polymerization of different functional monomers, including butyl/propyl vinyl ether and glycidyl isopropyl ether. The investigation of immobilization of the photosensitive moieties will be evidenced by FTIR, UV-Vis, TGA and XPS.

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SUSTAINABLE CURING BY PHOTOINDUCED FRONTAL POLYMERIZATION IN THE PRESENCE OF BIOFILLERS

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Frontal polymerization, characterized by a self-sustaining reaction triggered by an initial stimulus forming a localized reaction zone, referred to as the "polymerization front," is categorized into three types: thermal frontal polymerization, photoinduced frontal polymerization, and isothermal polymerization. The unique attributes of photoinduced frontal polymerization offer diverse applications not easily achievable with traditional batch processes, exhibiting superior time, energy, and cost efficiencies due to its rapid reaction rate and low energy input [1].

Despite these advantages, certain constraints exist. Photoinduced frontal polymerization requires highly reactive monomers for self-propagation, leading to unintended spontaneous polymerization in some monomer systems at or near ambient temperature. Another significant challenge is the effective mitigation of heat loss from the front to the surroundings. Furthermore, numerous polymerization motifs encounter issues such as undesired termination reactions or slow background gelation from a chemical perspective [1, 2].

In this work we present preliminary results on the curing of thick samples and samples buried in dark areas by photoinduced frontal polymerization of acrylic monomers (as sketched in Figure 1). The addition of natural fillers (e.g., wood powder and cellulose fibrils) was investigated. Characterization was performed by using FT-IR, UV-Vis and DMA instruments. In addition, the optimization of the process is discussed considering thermal effects, reaction mechanism, type of formulation, and environment and process conditions.

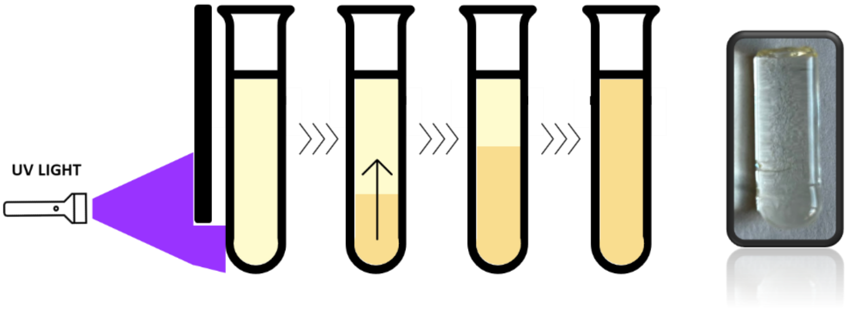

Figure 1. Photoinduced frontal polymerization process.

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ESPERANTO
Enhancing the Sustainability of PhotopolymERs ANd phoToinduced prOcesses

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The synthesis and characterization of a castor oil-based photoinitiator as a sustainable material

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During recent advances in the field of UV coatings and printing inks, researchers have tried to shift from less sustainable processes to more sustainable processes. Talking about sustainability, first and foremost concept that comes to mind is replacement of petrochemical products with biobased products. Traditional photoinitiators (PIs) that are being used could have potential health problems not only for humans but also for biota. The conventional use of photoinitiators (PIs) has raised concerns regarding potential health hazards for both humans and the environment. These PIs pose a risk of migration, especially when incorporated into biomaterials and food packaging, potentially leaching harmful substances into the food products [1, 2]. In biobased products, nature has bestowed us with cellulose, lignin and vegetable oils. Among these, Castor Oil emerges as a naturally occurring polyol with inherent double bonds and carboxylic group functionality. Harnessing these attributes, the focus is on transforming Castor Oil into a biobased product by substituting its -OH group(s) with -SH. This strategic modification not only renders Castor Oil conducive for biobased applications but also introduces the potential for self-initiation, even at room temperature. The innovative approach of utilizing castor oil and a Thioxanthone derivative [3] enables an esterification reaction, producing photoactive castor oil for our subsequent preparation of sustainable photopolymers [4]. This ease of application aligns with the overarching goal of exploring possibilities for curable coatings that balance economic considerations with biobased principles. The intersection of sustainable practices and technological innovation opens new horizons for the synthesis of coatings and inks that not only meet high-performance standards but also contribute to a greener and more environmentally conscious future.

Keywords: Biobased photoinitiator, Thioxanthone, Castor oil

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Enhancing the Sustainability of PhotopolymERs ANd phoToinduced prOcesses

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POLYMERIC/OLIGOMERIC PHOTOINITIATORS

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In the last years, the design and development of new photoinitiators (PIs) is gaining market interest due to the large amount of photoinitiators that have been banned or are going to be banned as toxic or reprotoxic. In particular, the reactivity to LED lamps was one of the main characteristics wanted as well as the low post-cure yellowing.

For sensitive applications, such as food packaging, other then good reactivity and lower yellowing also low migration of the photoinitiators into the food is required.

In this regard, polymeric/oligomeric and acrylated photoinitiators were extensively explored to give the best performances in migration conditions.

Several efforts were made in our lab in developing novel classes of polymeric/oligomeric photoinitiators able to reach the limit of zero migration and showing increased performance under LED lamps (more preferably in the range of 350-400 nm) as well as a low post-cure yellowing.

In this poster, we will present the reactivity of a new class of polymeric PIs. The reactivity of the novel compounds was evaluated in clear and pigmented compositions, giving enhanced performance compared to the current commercial compounds.

NANOPARTICLE EFFECT ON SCRATCH AND YELLOWING RESISTANCE OF UV CURABLE WOOD COATINGS

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Coating systems can be divided into different groups according to the curing mechanism and usage areas. UV Curable systems are a very important and developing part of coating systems because of the advantages they provide [1].

In recent years, the usage of nanoparticles has become of great interest in the coating industry to obtain functional coatings. Functional coatings are coatings that applied to surface to gain some special properties such as scratch and UV resistant. [2,3]. Especially for wood coatings, the biggest and undesirable problems are scratch and yellowing problems. There are some different ways to eliminate this problem, one of them is using light stabilizers such as; UV absorbers, HALS (Hindered amine light stabilizers) and antioxidants [4-6] and the other one is usage of nanoparticles.

In this study, an alternative approach was used to improve the scratch and yellowing resistance performance of coatings instead of adding nanoparticles to the formulations. UV-curable wood coating formulations were developed, applied to wood panels and after curing, their performances were tested (gloss, adhesion, hardness, scratch) and compared to each other and standard formula. The surface properties of the coatings were also examined with Scanning Electron Microscopy (SEM). In addition, yellowing resistance of coated panels were tested with accelerated weathering test device and the obtained data were compared with standard formula and each other.

Keywords: UV curing, wood coatings, scratch resistance, yellowing resistance, nanoparticles

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Photocrosslinking of ethylene-vinyl acetate (EVA)–polyethylene-octene (POE) copolymer containing halogen-free flame retardants

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Photocrosslinking of polymers for industrial applications show undoubted advantages related to the mild conditions needed and the economical equipment. However, some issues include: the use of (i) mercury lamps as light sources, which poses concerns about safety and energy consumption, (ii) typical additives, such as halogen-free flame-retardant fillers (HFFR) are powdered materials, which can scatter UV photons and avoid a deep penetration of the light. In this study, we explore the UV-curing of an innovative EVA-POE blend containing hydrotalcite and aluminum hydroxide as HFFR in the presence of a 370-nm UV LED, namely Ekopren® XI1321, a plastic used as coverage for electric cables. Two commercially available photoinitiators (benzophenone and ethyl Michler's ketone) were analyzed as well as two crosslinking coagents widely used in industry, that is, triallyl cyanurate and trimethylolpropane trimethacrylate. A comparison with pure EVA and LDPE was performed to show a higher cross-linked content of the proposed blend, even in the presence of light scattering mineral fillers at high concentration.

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COUMARIN-3-OXOACETIC ACID METHYL ESTERS: PHOTOINITIATORS FOR UV-VISIBLE FREE RADICAL AND CATIONIC PHOTOPOLYMERIZATIONS

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The high electron-transfer quantum yields of coumarins make them attractive candidates for designing efficient PIs.[1,2] In this study, three coumarin-3-oxoacetic acid methyl esters (COAEs) which exhibited strong ultraviolet visible absorption in the range 300–500 nm were synthesized and studied. Real-time fourier transform infrared (RT-FTIR) and photo-differential scanning calorimetry (photo-DSC) experiments showed that these PIs could be used as Norrish I photoinitiators and Norrish II photoinitiators to initiate free radical polymerization (FRP) of acrylate monomers, and they also can be used as photosensitizers of iodonium salts and sulfonium salts for cationic photopolymerization (CP) of epoxy and oxetane monomers. Furthermore, they can initiate the deep curing of Tri-(propylene glycol) diacrylate (TPGDA) at acceptable low concentrations of 0.01 wt% and approached to a depth of 9 cm after irradiation with a 415 nm or 450 nm LED light source for 5 minutes. Moreover, the COAEs exhibited acceptable photobleaching, which is in favourable of colourless applications of photopolymerization. The photochemical and photophysical properties of the COAEs were also studied with absorption and fluorescence spectroscopy, electron spin resonance, cyclic voltammetry experiments and photoinduced decarboxylation experiments to determine the photoinitiation mechanism. Additionally, cytotoxicity experiments were carried out, and the results showed that the COAE-N had good cytocompatibility. Therefore, the exceptional polymerization properties of COAEs offer promising prospects for FRP and CP applications. Additionally, their efficient photobleaching characteristics make them highly suitable for deep photopolymerization applications. Moreover, the low cytotoxicity of COAEs suggests significant potential for biomedical applications such as dental restoration.

Keywords: coumarin derivatives, free radical polymerization, cationic photopolymerization, photobleaching, sulfonium salts, deep curing

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Coumarin-3-oxoacetic Acids as Amphiphilic Photoinitiators for Free Radical and Cationic Photopolymerizations with UV–Vis LED Irradiation

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High-performance photoinitiators (PIs) play a crucial role in photopolymerization. Compared with traditional photo resource mercury lamp used in photocuring, ultraviolet–visible (UV-Vis) light-emitting diodes (LEDs) have attracted growing attention due to their environmental friendliness, low heat emission and long lifetimes. Recently, PIs that match the UV-Vis light sources have been extensively exploited, including coumarins, benzophenones, camphorquinones, thioanthrones, phenothiazines, and several metal organic compounds. Coumarins, derived from fungi, bacteria, and plants, are considered green renewable resources and find applications in food processing, biomedicine, and optoelectronics. The high electron-transfer quantum yields of coumarins make them attractive candidates for designing efficient PIs.[1, 2] Herein, three coumarin-3-oxoacetic acids (COXAs) as amphiphilic PIs used in photocured technology were synthesized and studied. As one kind of amphiphilic PIs, COXAs can be used both in traditional organic photocured technology and water-based photocured technology which is more in line with the tenets of green chemistry as it eliminates volatile organic gas (VOCs) emissions. These PIs exhibit good UV absorption in the range of 300-500 nm. The real-time fourier transform infrared (RT-FTIR) and photo DSC experiments were operated. The results showed that not only can they be used as Norrish I PIs or Norrish II PIs to initiate free radical polymerization (FRP) of acrylate monomers but also sensitize iodonium salt and sulfonium salt to initiate cationic polymerization (CP) of epoxy and oxetane monomers. Moreover, they can initiate the deep curing of Tri-(propylene glycol) diacrylate (TPGDA) in in the very low concentration which is 0.01%. The curing depth can exceed 9 cm within 5 min irradiated by 415nm LED (100 mW • cm^{-2}). Furthermore, they can also initiate the deep curing of the water-soluble monomer polyethylene glycol (400) diacrylate (PEG (400) DA) to approach to the same depth as TPGDA at the same irradiation condition, even in various proportions of water. Meanwhile, COXAs exhibit acceptable photobleaching phenomenon. The photochemical and photophysical properties of COXAs were studied in terms of absorption, fluorescence spectroscopy fluorescence quenching, electron spin resonance, liquid chromatograph mass spectrometer and cyclic voltammetry experiments to disclose the photoinitiation mechanism. Additionally, cytotoxic experiments were carried out, and the results showed that the three PIs, especially COXA-N, had good cytocompatibility. In total, this work highlights the potential of a series of novel visible light initiators, COXAs, exhibiting efficient photobleaching, excellent depth curing, high conversion rates, thermal stability and low cytotoxicity, which are promising prospects for different photocuring applications.

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Sub Diffractional STED-Inspired Cationic Lithography

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Stimulated emission depletion (STED) broke the diffraction limit of resolution in fluorescence microscopy and it has been proposed that a STED-confined excitation volume should be equally applicable to spatially control chemical reactions on the nanometre scale.[1] Meanwhile, this prediction has been experimentally realized using free radical polymerization of mostly (meth)acrylates.[2-4]

In this contribution, we will present concepts of how to achieve sub 100 nm structure sizes in STED-inspired epoxide cationic lithography by using a modified system of photosensitizers and initiators. In particular, we use thioxanthones as sensitizers and a sulfonium salt as initiator. The thioxanthones turned out to be optically depletable within the triplet system by transient state absorption depletion (TAD).[5, 6] Making use of this depletion mechanism in the outer rim of the excitation focus, we were able to write sub-diffractional, 125 nm wide epoxide features with isopropyl thioxanthone,[7] and, most recently, even sub-100 nm features using 2-chlorothioxanthone.

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In Depth characterization of photopolymerized materials by Confocal Raman Spectroscopy.

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Confocal Raman Microscopy (CRM) is a powerful microscopic and spectroscopic technique to fully characterize the intrinsic chemical properties of thin and thick organic materials. The confocal analysis allowed us to achieve a highly solved spatio-temporal description of chemical composition on the surface and more importantly along the depth of the material. This could subsequently be correlated to the history of formation and "life" of the analyzed coating films and materials.

Few representative examples will be presented during this talk to describe the methodology and resolution in depth and correlation with more established methods frequently used in the analysis of photopolymers conversion such as RT-FTIR, limited nevertheless to thin films.

In brief, CRM is presented as a powerful complementary technique to achieve useful chemical and photochemical information in the function of the starting material and/or resin composition. This brings clearness for the optimization of formulations applied on different 3D and 4D printing, techniques nowadays used in a growing myriad of applications to bring response to stricter environmental regulation.

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BIOINSPIRED MULTIFUNCTIONAL COATINGS BY UV-NANOIMPRINT

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Nature can impart extraordinary properties to surfaces, such as super hydrophobicity or anti-reflectivity, through the synergistic work of hierarchical structures with nano and micro features and correct functional groups. [1-6] Two main approaches have been used to replicate nature's features: bottom-up self-assembly and top-down lithographic techniques. [7, 8] This work will focus on the use of UV-nanoimprint lithography (UV-NIL) to copy natural surfaces. Several papers have reported successful replication of natural surfaces, such as lotus leaf, rose petal, and moth eye, using liquid precursors and UVNIL, resulting in good hydrophobicity or anti-reflectivity properties. [9-13] These functional surfaces, however, are organic in nature and not specifically robust. A first objective of our work it thus to develop nanocomposite formulations using inorganic phases to create hard surfaces that are far more wear resistant than the polymer surfaces.[14] Multiple challenges associated with the addition of nanoparticles in UV-curing liquid resins which would compromise processability, such as a huge viscosity increase and light scattering will be addressed.[15] This work goes also beyond the examination of the hardness and wear resistance of the coating. It also delves into other properties, such as its effectiveness as a barrier against the diffusion of small molecules such as water or oxygen.

A further aim of this work is to implement the UV curable nanocomposite formulations for R2R processing of large surfaces with patterns replicated from nature. The focus will be on the impact of photocuring kinetics and formulation viscosity on the accuracy of lithographic details, as well as the development of a fluorine-free coating with self-cleaning and antireflective properties using R2R UVNIL processing.

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Polymer/Nanoparticle Hybrid Coatings with the Graded Nanostructures via Controlled UV Curing

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The utilization of polymer dormant with carbon-iodine (C-I) terminals in photo-controlled radical polymerization has enabled the formation of bi-continuous microphase-separated nanodomains. A polymeric dormant can be reactivated via iodine-mediated radical polymerization, that allows the controlled chain extension to give block copolymers. A glycidyl-containing polymeric dormant (**PGMA-BA-I**) was used in the preparation of an organic-inorganic hybrid UV-cured film with zirconia nanoparticles.

The polymeric dormant, **PGMA-BA-I**, was dissolved in an acrylate monomer along with zirconia nanoparticle dispersion. A triacrylate crosslinker and photocatalysts triphenylphosphine (PPh_3) and/or 10-phenylphenothiazine (PTH) were added and then bar coated on PET film before UV irradiation. Cross-sectional transmission electron microscope (TEM) images of the coatings revealed the selective incorporation of the zirconia nanoparticles in the epoxy (GMA) domain. In addition, a gradient-arranged zirconia nanoparticles coating morphology was obtained by utilizing triphenylphosphine (PPh_3) as the catalyst at low equivalent amounts. Furthermore, the domain size and the gradient direction can be tuned by using 10-phenylphenothiazine (PTH) photo-redox catalyst. The optical properties, especially the reflectance, that the different nanostructures exhibit was also evaluated.

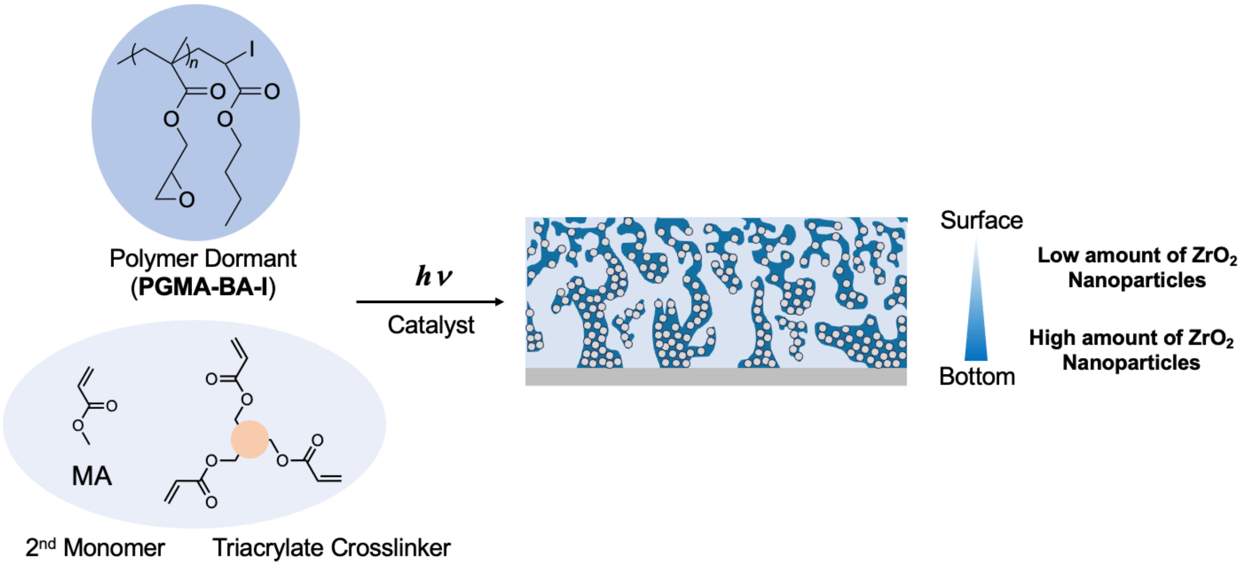

Fig. 1 Preparation scheme and illustration of the photocured hybrid coating with gradient structure.

Expanding the limits of aliphatic photoinitiators based on α-ketoesters for free radical photopolymerization

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Free radical photopolymerization of (meth)acrylate based formulations is considered one of the most important technologies in radiation curing industry due to the high energy efficiency and fast curing times. Therefore, it is frequently used for protective and decorative coatings, biomedical and dental applications. Common industrially used radical photoinitiators (PIs), e.g. benzophenone, contain benzoyl chromophores as a key moiety due to its excellent absorbance in the UV-Vis region. However, the use of these state-of-the-art photoinitiators in food or medicinal products is becoming more and more regulated as their degradation and recombination products are suspected of being mutagenic or cancerogenic to humans.[1,2]

Herein, we explored a new generation of aliphatic photoinitiators based on α-ketoester moieties due to their high biocompatibility.[3,4] Therefore, we envisioned “crowded PIs”, containing more than one photocleavable group per molecule. Compared to the industrially used benzophenone-amine photoinitiator system, the developed α-ketoesters show enhanced photoreactivity, monomer conversion and higher curing speed in (meth)acrylate formulations and (meth)acrylate-based hydrogels. Furthermore, the applicability of α-ketoesters for the highly selective and biocompatible thiol-ene photoconjugation is demonstrated, making the novel set of α-ketoester photoinitiators potential substituents for biomedical applications.

Acknowledgements

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The Possibilities and Challenges of Photobase Generators for Oxa-Michael Reactions

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Step-growth polymerization is still highly valued in the field of additive manufacturing to produce tougher materials compared to free radical polymerization. Thiol-ene chemistry sees widespread use in this application, yet, it has its drawbacks, such as the availability of thiols, their strong odor, and a low storage stability.[1,2] Switching from sulfur to oxygen enables a wider variety of available monomers without the odor. The oxa-ene reaction is a base catalysed Michael-type reaction with recent research finding highly effective Lewis-base catalysts.[3] Our work includes the transition from a free base catalysed system to light triggered systems using our novel Lewis photobase generators. These were applied for both model reactions and polymeric formulations. Former allowed for an in-depth investigation of the mechanism alongside the high storage stability of the system. As the reaction speed was higher at elevated temperatures, our polymeric system was a perfect fit for Hot Lithography yielding 3D-printed parts with high resolution.[4]

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Sub-diffractional optical lithography of π-conjugated polymers

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Stimulated emission depletion (STED) proved to break the diffraction limit of resolution in fluorescence microscopy. Besides, it was proposed already in 1999 that the STED-confined excitation volume should be applicable to spatially control photochemical reactions on the nanometre scale.[1] Meanwhile, this prediction has been experimentally realized using two-photon induced radical polymerization of negative tone resists, most of them (meth)acrylates.[2-4] Progress has been made in finding an optically depletable starter which shows only low autofluorescence in the visible spectrum, so that it can be used to construct scaffolds for biomedical applications which do not optically interfere with fluorescent tags.[5] Lately, we succeeded to transfer this concept to cationic polymerization of epoxides.[6]

Most recently, we are now applying STED-inspired two-photon lithography to π-conjugated polymers.[7] We found photoinitiators for oxidative polymerization of EDOT (3,4-Ethylenedioxythiophene) that are excitable with two photons of 780 nm light and depletable with 660 nm. Sub-100 nm lines were successfully written. Our results bear potential for prototyping sub-100 nm organic electronic devices.

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3D-PRINTED EOSIN Y-BASED HETEROGENEOUS PHOTOCATALYST FOR ORGANIC REACTIONS

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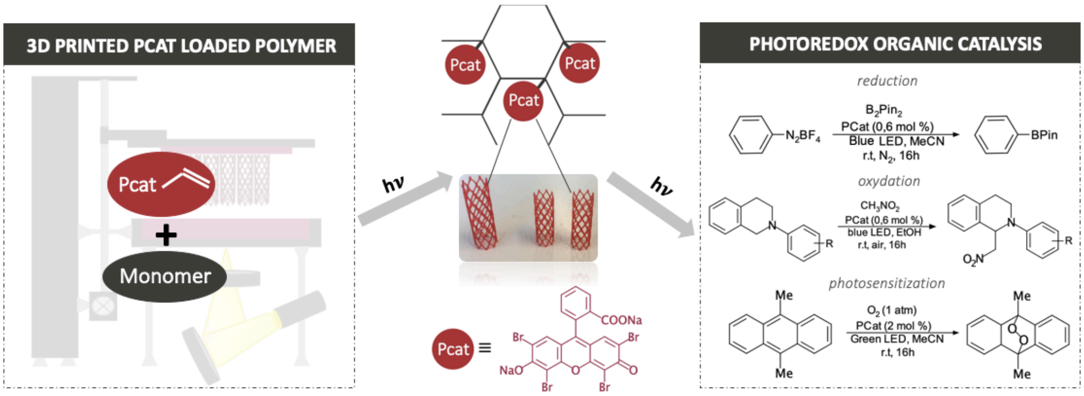
Photoredox catalysis for organic transformation has been considered as a powerful tool in organic synthesis since its revival in 2008 [1-2]. This innovative field of chemistry relies on the excitation of a photocatalyst (PCat) giving an excited state with unique properties, including the ability to transfer electrons or to transfer energy. However, most of the photocatalysts are prepared and used in homogeneous phase which limits the applications since the photocatalyst is not recover at the end of the reaction. The solution is to switch from homogeneous to heterogeneous catalysis using a support with high accessibility to PCat [3-4]. The approach of this project is the fabrication and evaluation of new 3D printed polymer-based supported photocatalysts [5-6]. Polymeric supports are synthesized via free radical polymerization to yield a recyclable hierarchical polymeric network including a non-toxic PCat (eosin Y) covalently bounded. The photocatalytic activity of this new object was then evaluated through model organic reactions in oxidation, reduction, and photosensitization.



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DIGITAL LIGHT PROCESSING OF MULTIFUNCTIONAL MAGNETO-BASED NANOCOMPOSITES

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The revolution of 4D printing allows combining smart materials to additive processes to create behavioral objects that are able to respond to external stimuli, such as temperature, light, electrical or magnetic fields. It follows then, that the synthesis of novel printable responsive-materials is currently at the bedrock of academic research. Besides, an ever-increasing attention is also being given to the synergetic incorporation of nanofillers within printable matrices so as to craft and modulate the functional properties of the resulting composites in a multiscale approach, where both embedded fillers and polymer matrices play an active role.[1-2]

Within this framework, a method for fabricating multifunctional polymer nanocomposites by means of Digital Light Processing (DLP) 3D printing is here presented. In particular, the approach entailed integrating two distinct functions into a photocurable poly(ethylene glycol) diacrylate (PEGDA) resin, namely, i) iron oxide nanoparticles (Fe_3O_4 NPs), to enable the DLP printing of magneto-reactive components and ii) silver nitrate ($AgNO_3$), as a precursor for the photogeneration of silver nanoparticles (Ag NPs) during a post-printing UV-irradiation process,[3] to give to the printed nanocomposites additional electrical properties and bactericidal traits. The printing parameters were optimized to reproduce highly complex 3D-architectures, the printed nanocomposites have been fully characterized and their multifunctional properties were demonstrated.

Finally, some insights will be given on the possibility to further expand the applications of 3D/4D printed magnetic nanocomposites exploiting the assembly or patterning of the nanofillers during the printing process through the use of a modified commercial DLP printer allowing to control both the intensity and the spatial direction of the applied magnetic field.[4] This may envisage the fabrication of a new class of nanocomposites with superior functional properties given by their unique anisotropic architectures.

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VAT PHOTOPOLYMERIZATION OF SWCNT-BASED SOFT COMPOSITES WITH HIGH MIXED ION-ELECTRON CONDUCTIVITY ENABLED BY IONIC LIQUIDS

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Vat photopolymerization (VPP) is a UV-light-assisted additive manufacturing technique capable of producing high-resolution parts with excellent surface finishes and micron-scale features. VPP has been effectively used to fabricate thermoelectric, bioelectronic, energy storage, sensor and actuator devices[1]. One of the next-generation functional materials proposed for the fabrication of these devices is mixed ion-electron conductors (MIECs), capable of efficiently transporting and coupling both ionic and electronic charges[2]. We have recently demonstrated the compatibility of imidazolium-based ionic liquids (ILs) with specific photopolymerizable monomers and cross-linkers. This compatibility allowed us to formulate a photopolymer composition for VPP of ionic conductive gels[3]. The insertion of single-walled carbon nanotubes (SWCNT) into photopolymer compositions for VPP can provide sufficient electronic conductivity for the 3D printed material with a low electrical percolation threshold. However, the VPP of SWCNT composites is a long-standing challenge, as SWCNTs in dispersions typically agglomerate in bundles by van der Waals forces. Moreover, SWCNT dispersions are poorly transparent to UV light and exhibit non-Newtonian behavior due to forming an elastic nanotube network. Considering these aspects is crucial for successful 3D printing of SWCNT dispersions using UV-assisted techniques.

Here, we demonstrate that adding 1-alkyl-3-methylimidazolium tetrafluoroborate [AlkylMIm][BF_4] ILs in photopolymer compositions allowed dispersing SWCNT bundles, provided ionic conductivity in the resulting 3D printed material, and accelerated the photopolymerization. Using polar monofunctional monomers N-vinylpyrrolidone and 2-hydroxyethyl methacrylate with polyethylene glycol methacrylate (M_w ~ 750) as a cross-linker allowed avoiding syneresis of IL from polymer matrix during UV and thermal post-curing process.

We showed that the dispersion stability increased with the increase of alkyl tail length of IL cation and obtained the following stability order: [EthylMIm]<[ButylMIm]<[HexylMIm]~[OctylMIm]. The increase of the conversion after applied thermal post-curing was shown by dynamic-DSC and FTIR. Rheology analyses showed that the photopolymer compositions with SWCNT concentration lower than 0.4 wt.% exhibit shear thinning behaviour with dynamic viscosity (<10 Pa*s) at a shear rate of 10 s^{-1}, appropriate for VPP. The impact of SWCNT on photorheology curves, specifically the gel time and plateau of storage modulus, was also examined.

Equivalent circuits were employed to separate the ionic and electronic conductivity by fitting Nyquist plots obtained through impedance spectroscopy. Analyzing the photorheology and working curves of the photopolymerizable IL-SWCNT dispersions allowed us to successfully 3D print MIECs reinforced with high SWCNT content (up to 0.4 wt%) with enhanced thermal, electronic and ionic conductivity, and mechanical properties.

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3D PRINTABLE, SELF-HEALING AND IONIC CONDUCTIVE HYDROGEL FOR SELF POWERED TACTILE SENSORS

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Smart sensors based on conductive hydrogels have shown a remarkable potential whenever a link between the "soft" human world and the "rigid" electronic one is required, in fields like wearables and soft robotics [1,2]. However, conventional manufacturing technologies, such as casting processes, limit the shapes obtainable and consequently the applications[3].

Here, a photocurable double network poly(vinyl alcohol)/Acrylic Acid (PVA/AAc)[4] hydrogel was doped with Sodium Chloride (NaCl) to improve its ionic conductivity. The resulting hydrogel (PVA/AAc/NaCl) exhibited high stretchability, electrical responsiveness to external mechanical stimuli and autonomous self-healing. In addition, formulation reactivity to UV light makes it an optimal choice for 3D printing. Indeed, complex structures that enhanced mechanical stress sensitivity were fabricated exploiting Digital Light Processing (DLP) 3D printing technique. Moreover, the application of PVA/AAc/NaCl hydrogel as electrolyte in a Laser Induced Graphene (LIG) based supercapacitor [5] expanded its versatility bringing to the production of customizable self-powered and self-healing multifunctional strain sensors.

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NEW ONE-COMPONENT IODONIUM PHOTOINITIATORS WITH ADVANCED CHROMOPHORES FOR CATIONIC VAT 3D-PRINTING

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Vat 3D printing is an excellent alternative to traditionally preparing polymer 3D objects, reducing costs, and increasing the resolution of the objects. However, the application of cationic vat 3D printing is still limited by a number of inconveniences such as the lack of suitable photoinitiators absorbing in the emission range of light sources used in printers (about 405 nm).[1]

The most commonly used iodonium salts are diaryl derivatives proposed by Crivello in the 70s. They absorb poorly above 300 nm and need photosensitizers or special light sources to initiate polymerization efficiently.[2] Therefore, the development of advanced iodonium salts that absorb in the longer wavelengths is essential. They must also efficiently generate super acid.

Our new innovative chromophore designs allow iodonium salts to be obtained in a selective manner which was previously impossible for the more sophisticated chromophores.[3] Moreover, a double bond was used in these chromophores, and, among others, we obtained the first symmetric iodonium salts containing such moiety.[4] Such advances in the structure of iodonium salts (possible by our design) have produced compounds with excellent absorption properties reaching into the visible range. These new iodonium salts are able to photolyze efficiently at 365 nm and 405 nm LED irradiation and can photoinitiate the cationic polymerization process of such monomers as epoxides and vinyl ethers. It was possible to study the substituent effects due to the easily modifiable structure of the chromophore, which allowed for a better understanding of sophisticated iodonium salt properties. This design leads to a great improvement in photoinitiating properties so that our salts can be used in such advanced applications as cationic vat 3D printing.

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USING ORTHOGONAL PHOTOREACTIONS TO LOCALLY CONTROL DYNAMIC BOND EXCHANGE REACTIONS

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Using light to control structural/mechanical properties and the formation of polymers is one of the most powerful tools in polymer science. It enables the production of specific, adaptable and reliable polymers and can be used for the formation, degradation and functionalization of polymers. Moreover, we have shown in our recent work that it allows to locally introduce dynamic properties into photopolymer networks. Photolatent catalysts are a versatile concept to spatiotemporally control the rate of bond exchange reactions in dynamic polymer networks at increased temperatures. The usage of photoacid generators as latent transesterification catalysts leads to the local formation of Brønsted acids upon UV exposure, which can efficiently catalyze thermo-activated transesterification reactions. By utilizing a dual-wavelength 3D printer (operating at 405 and 365 nm) the orthogonality between the curing (405 nm) of a thiol-acrylate photopolymer and the activation reaction of the catalyst (365 nm) (Figure 1) was exploited.[1, 2] This enabled the fabrication of soft active devices, which undergo locally controlled topology rearrangements at elevated temperatures and also the preparation of positive toned photoresists. More recently, the concept of chemical amplification was used to control the dynamic behavior in thiol-ene networks. Therefore, photolatent sulfonic acids were synthesized to catalyze the deprotection reaction of a tert-butoxycarbonyl group, which was introduced to mask the hydroxy groups of a vinyl monomer.[3] Simultaneously, the formed acid served as a catalyst for thermo-activated exchange reactions between the deprotected hydroxyl and ester moieties in an orthogonally-cured (450 nm) thiol-ene photopolymer.

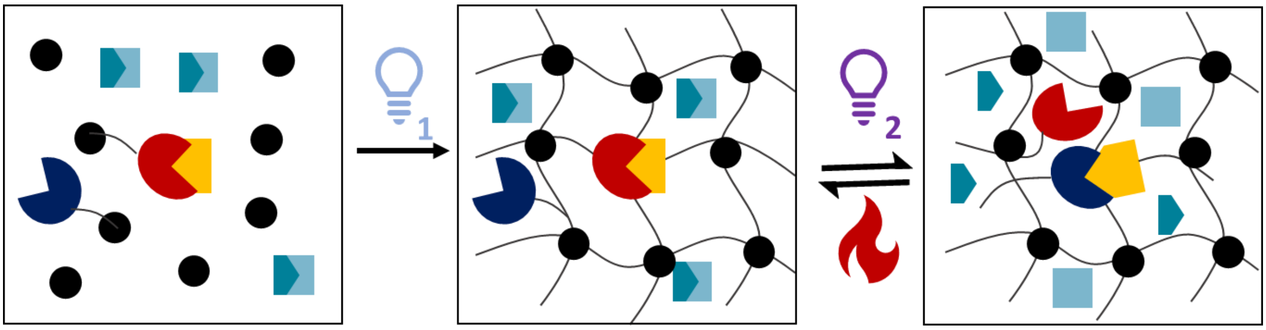

Figure 1. Orthogonality between network formation and catalyst activation to allow dynamic bond exchange.

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NATURAL-BASED PHOTOCURABLE FUNCTIONAL MATERIALS FOR DIGITAL LIGHT PROCESSING

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The increasing demand for additive manufacturing, particularly digital light processing (DLP) printing, has raised concerns regarding its environmental impact. Conventional materials used in DLP printing, such as petroleum-based resins, often pose challenges in terms of sustainability, resource depletion, and waste generation. To address these issues, it is required to explore sustainable alternatives derived from natural sources[1].

Natural polymers have gained significant attention for printable ink development due to their availability, low cost, biodegradability, and compatibility with various printing techniques. The formulation of natural polymer-based inks involves careful consideration of their rheological properties, stability, and printability, while maintaining biocompatibility and environmental sustainability[2]. This work highlights the key factors influencing ink development, including material selection, ink formulation, and process parameters optimization, to achieve reliable and high-quality 3D printed objects. Thus, different reactive diluents have been tested in soybean oil-based inks to optimize viscosity to allow a DLP printable formulation. The photopolymerization process of the obtained materials is comparable with the one of commercially available resins, while maintaining high biorenewable carbon content and presenting high quality in printing parts.

Further, the incorporation of fillers into natural polymer-based inks has opened up new possibilities for functionalizing printed objects[3]. Along this work, different functional materials including thermochromic ionic liquids, conductive particles or photoluminescent salts have been successfully incorporated in soybean-oil based polymers. The influence of filler content in the UV curing process, ink viscosity, thermo-mechanical properties and functional response have been investigated. This work sheds light on the advancements in natural polymer-based inks for additive manufacturing, specifically targeting DLP technology, and emphasizes the potential of integrating fillers to expand the functional capabilities of 3D printed objects. The findings presented in this abstract contribute to the broader understanding of materials development for additive manufacturing.

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DESIGN FOR DISASSEMBLY – USING A MULTI MATERIAL APPROACH IN 3D PRINTING FOR EASIER RECYCLING STRATEGIES

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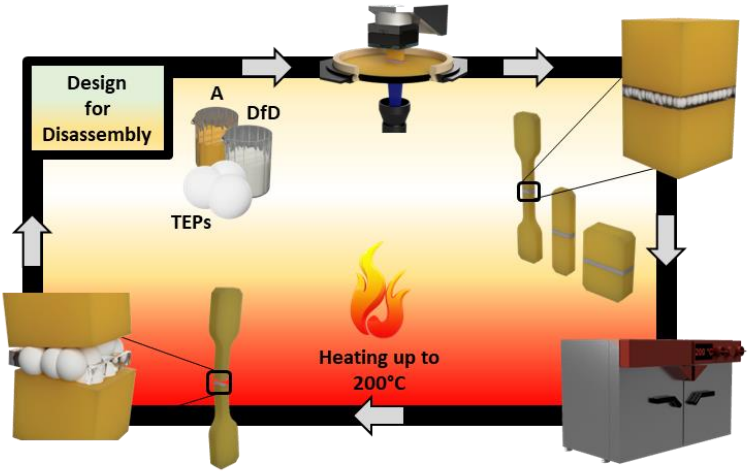

***Figure 1:** Concept of Design for Disassembly (DfD)*

Due to advancing technology, a wide range of electrical devices, including consumer electronics, and batteries, are being rapidly developed and increasingly used in daily life. These components contain crucial resources, including noble metals and rare earth elements, that must be reclaimed for future use. Yet, achieving a higher device performance necessitates a complex and highly integrated architecture to increase efficiency. This makes it more difficult to recycle such systems and to regain the valuable materials. Additive manufacturing, commonly known as 3D printing, has the potential to address this issue due to its distinct capabilities to produce parts within the micron range, the freedom of geometrical design, and the ability to process thermoset polymers. [1]

Herein we present a first step to use additive manufacturing to create better recyclable components. By introducing the concept of “Design for Disassembly” (DfD) we aim to highlight the potential for products, or multi-material components to be separated and recycled with ease. Using a multi-material approach, we printed a thin layer of a Disassembly material (DfD-material) within two blocks composed of Material A (Figure 1). The DfD-material should not affect the (thermo)mechanical properties of the component. However, upon activation with a thermal impulse, it should facilitate the separation of the component. Additionally, Thermally Expandable Particles (TEPs) were incorporated into the DfD-material to enhance separation.
To assess the influence of the DfD-material, various specimen groups (including those with and without the DfD-material) were printed and analysed for their (thermo)mechanical properties, and the ability to be disassembled.

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OPTIMIZATION OF PRINTING PARAMETERS TO OBTAIN HIGH-RESOLUTION OBJECTS FOR THE DENTAL INDUSTRY

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Photopolymerization is a polymerization technique in which monomers or prepolymers are transformed into polymers by utilizing light radiation, often of a specified UV or Vis wavelength. During photopolymerization, the photoinitiator introduced to the reaction system becomes decomposed by light energy absorption. The ensuing free radicals or radical ions activate the monomers, which subsequently react with one other to create chemical bonds, culminating in the development of a three-dimensional polymer network [1]. Photopolymerization is frequently employed in 3D printing applications, which is used in aerospace, defence, art, and design, architecture, biology and many more, and is becoming increasingly popular in surgery and dentistry. With advances in 3D imaging and modelling technologies such as cone beam computed tomography and intraoral scanning, as well as the relatively long history of the use of CAD CAM technologies in dentistry, the technology will become increasingly important [2]. There are various advantages to using photocurable polymer materials in 3D printing for dental applications over traditional production methods. These include decreased material waste, greater design flexibility, quicker production times, as well as improved mechanical qualities in final dental restorations [1]. 3D printing technology is used in dentistry for a variety of purposes, including the creation of drill guides for dental implants, the development of physical models for prosthodontics, orthodontics, and surgery, the fabrication of dental, craniomaxillofacial, and orthopaedic implants, and the creation of copings and frameworks for implant and dental restorations [2].

In this work, potential use of compositions containing the new photoinitiators in 3D printing for broad-spectrum of dental applications, as well as the optimization of 3D printing conditions have been presented.

Acknowledgements

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NOVEL BIODEGRADABLE SOYBEAN OIL-BASED COMPOSITES OBTAINED BY LCD 3D PRINTING

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The interest in developing a circular economy through the adoption of new manufacturing technologies and the use of innovative materials deriving from renewable resources is attracting considerable attention. Additive manufacturing (AM), or 3D printing, is one of the most rapidly growing technologies, as it enables the manufacturing of prototypes or parts with complex geometries in a cost-effective way and with reduced consumption of materials. Among the different AM techniques, VAT-polymerization (VP), allows to realize objects with high complexity and to achieve the highest printing resolution. However, the use of this technique is limited by the low number of sustainable photopolymerizable resins. In fact, the highest number of commercially available 3D printable photopolymers concern acrylates and epoxides derived from fossil-based sources. Due to the increasing environmental concern, vegetable oils have attracted great interest, because they are renewable, biodegradable, and inexpensive. Moreover, they exhibit structural features that make them very attractive for developing a wide range of polymeric products, competitive from academic and industrial point of view, having properties comparable to the conventional fossil-based polymers. In this scenario, the aim of the present work was to prepare novel biodegradable soybean oil-based composites containing two different biofillers, coming from agro-wastes, by means of LCD 3D printing process. Given the great interest in using vegetable oil derivatives as the main component to develop UV printable resins, the study started by an in-depth investigation of the formulations based on AESO alone and in combination with reactive diluents, such as IBOMA and THFA. Once identified the best photocurable formulations in terms of viscosity and processability, bio-based composites were prepared by adding 5 wt.% of biofillers, a corn-derived product (GTF), and a wine-derived product (WPL-DH), respectively. The purpose was to use them as reinforcing agents, and to enhance the value of this bio-renewable feedstock, leading to the realization of 3D printed parts and to environmental benefits. Different biodegradable 3D printed composites were successfully obtained by LCD with increasing complex structure and increased final properties, from thermal to mechanical point of view.

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AGRI-FOOD WASTE VALORIZATION FOR DLP 3D PRINTABLE ADVANCED MATERIALS

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Every year, enormous amounts of agri-food waste are produced, which presents a significant issue from an environmental and financial standpoint. According to the circular economy's tenets, these wastes can be repurposed as secondary starting materials to create objects with added value.[1]

The present work is based on the extraction and functionalization of organic molecules, ranging from cellulosic components to anthraquinones, from Aloe Vera and aloe Arborescence Sardinian cultivation wastes. The extracted fractions are used as materials for the development of photocurable polymers suitable for light induced 3D printing (3DP).

Work done so far has focused on the extraction of micro cellulose semicrystalline particles (MC). On one side, MC has been functionalized to obtain acrylate microparticles that can act as fillers or crosslinkers in a photocurable formulation. Beside the simple use as natural filler, the choice of the correct copolymers enables the formation of covalent adaptable networks[2] (CANs) able to be reprocessed under external stimuli (e.g. temperature). The best printing conditions have been optimized for the production of samples and the ongoing study of the thermomechanical properties of the developed materials will disclose the CAN behavior of the developed materials.

On the other side, MC has been solubilized and functionalized using eutectic solvents[3] enabling the 3D printing of flexible polymers in which the cellulose chains act as crosslinker.

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Development of fracture tough dental materials containing ABA triblock copolymers for 3D printing applications

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3D printing is an attractive technology in dentistry, as it enables a fast and cost-effective manufacturing of customized dental materials. Moreover, the possibility to print several objects at once represents a considerable advantage. DLP (digital light processing) and SLA (stereolithography) are the most commonly used 3D printing technologies in dentistry in order to produce with high precision various materials such as tooth models, orthodontic workpieces (e.g. splints), wax models for metal casting and press ceramics, denture bases and denture teeth. The development of 3D printing denture bases is particularly challenging as these materials must exhibit high mechanical properties (high flexural strength and modulus) as well as high fracture toughness. Due to the low reactivity and high volatility of MMA, conventional MMA-based denture bases are hardly suitable for 3D-printing. Therefore, 3D printing resins mainly contain dimethacrylates. Unfortunately, networks resulting from the curing of dimethacrylate mixtures are typically brittle and not adapted for the preparation of tough denture materials. There is therefore a need for an efficient toughening technology that would be compatible with the 3D printing process. The pioneering work of Bates *et al.* regarding the incorporation of block copolymers (BCPs) as toughening agents in epoxy resins represented a major breakthrough.[1] Indeed, this approach enables a significant increase in fracture toughness without strongly impairing the flexural modulus and the glass transition temperature of the cured epoxy resins. Although this toughening technology was shown to be efficient in epoxy materials, it just led to a moderate increase of toughness if applied in dimethacrylate networks.[2] One of the reasons that has been given to explain this phenomenon, is the inhomogeneity of the networks that are obtained via radical polymerization of di(meth)acrylates. In this contribution, a technology based on the toughening of low crosslink-density dimethacrylate networks using BCPs will be described.[3] In order to obtain materials exhibiting a moderate crosslink density, a combination of a urethane dimethacrylate with a monofunctional (meth)acrylate was selected as a monomer mixture. Various triblock copolymers were used as toughener. The addition of such BCPs to the monomer mixtures has been shown to result in the formation of nanostructures via self-assembly. The fracture toughness of the cured materials was significantly increased. Results regarding the influence of various factors (nature of the monomers and of the BCPs, BCP content, crosslink density, etc.) on both the mechanical properties and the fracture toughness will be presented.

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Thiol-based Photopolymerizable Coating Enabling the Fabrication of Soft, Transparent, Patient-Specific Vascular Models with SLA 3D-Printing

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Abstract

Simulating endovascular procedures and studying hemodynamics with vascular phantoms aid in endograft selection and surgical planning. Ideally, a vascular phantom should be anatomically accurate, made in a soft material with properties as close as possible to vascular tissue, and sufficiently transparent for ease of visualization. However, achieving the convergence of these properties has proven challenging. Furthermore, no reports were found in the literature on post-processing treatments to improve the final finish of elastomeric SLA 3D-printed objects in general, let alone when complex hollow geometries are required. Here, we report the fabrication of real-sized patient-specific vascular phantoms with high anatomical fidelity and optical transparency, as well as mechanical properties closer to those of vascular tissue. These final properties were achieved by 3D-printing patient-specific vascular models with commercial elastomeric acrylic-based resins before coating with thiol-based photopolymerizable resins. Ternary thiol-ene-acrylate chemistry was found to be optimal. A PETMP/allyl glycerol ether (AGE)/polyethylene glycol diacrylate (PEGDA) coating with a 30/70% (PETMP-AGE)/PEGDA ratio applied on a flexible resin yielded elastic modulus, UTS, and elongation of 3.41 MPa, 1.76 MPa, and 63.2%, respectively, within the range of the human aortic wall. The PETMP/AGE/PEGDA coating doubled the optical transmission from 40% to 80%, approaching the 88% of the benchmark silicone-based elastomer. Higher transparency correlates with a decrease in surface roughness from 2000 to 90 nm after coating. Coated 3D-printed anatomical replicas are showcased for pre-procedural planning and medical training with good radio-opacity and echogenicity. Our overarching goal is to introduce the use of thiol-click chemistry for coating 3D-printed objects as a straightforward solution to some of the inherent limitations of photopolymer-based additive manufacturing, as exemplified in the case of the fabrication of unparalleled vascular phantoms.

Designing new Materials for 4D (Micro)printing

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4D printing has become a promising tool for the fabrication of dynamic and adaptive structures. During the last years, promising examples of defined 4D microstructures employing stimuli-responsive materials have been shown using two-photon 3D laser printing. Herein, we present our recent work on the field with emphasis on new responsive materials enabling the preparation of adaptive and structures. In particular, shape memory polymers as well as liquid crystal elastomers have been explored. In the first case, a simple and versatile formulation has been developed enabling complex microstructures with remarkable shape memory properties. Also, multi-responsive structures using photo responsive liquid crystal elastomers, are demonstrated. Furthermore, we have exploited the inclusion of dynamic and living bonds in a printable formulation enabling the creation of microstructures with „life-like" characteristics such as adaptability by tunable shape and mechanical properties. In addition, we demonstrated at the macromolecular sequence, specifically the positioning of the crosslinkable group, plays a critical role in both the printability and final properties of the printed material. We envision that the careful and precise desing of new printable materials will open new opportunities for the additive manufacturing of functional devices in the near future.

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Macromolecular Engineering: From Precise Macromolecular Inks to 3D Printed Microstructures. S.O. Catt, M. Hackner, J.P. Spatz, E. Blasco, *Small* **2023**, 2300844.

A DEVICE TO PROGRAM THE MICROSTRUCTURE OF MAGNETIC NANOCOMPOSITES DURING DIGITAL LIGHT PROCESSING (DLP)

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Within the realm of 3D printing, smart and functional materials is a blossoming research field. Indeed, their functional properties pertain to the ability to interact with the environment, responding to various external stimuli. As a result, the combination of additive manufacturing with smart materials is opening up exciting possibilities for creating constructs that can actively react to stimuli. Besides, an ever-increasing attention is being given to the synergetic incorporation of fillers within the printable smart matrices so as to craft functional polymeric composite materials. This approach allows to expand the relationship between form and properties and offers an attractive strategy to generate objects with functional and/or reinforced properties.

Potential applications of 3D printed composite constructs are further expanded if the embedded fillers can be manipulated, assembled, or patterned during the printing process, so as to induce well-ordered and/or anisotropic microstructures. The primary interest in printing objects presenting a microstructure (oriented and organized) is generally associated with the possibility to obtain objects with enhanced mechanical and functional properties. However, the precise spatial control and arrangement of embedded fillers within a material during the printing process presents significant challenges, making this research area largely unexplored in both academic and industrial domains.

Here, we present a magnetic device that can be easily adapted to most of light-driven 3D printers, and that allows to generate a homogeneous magnetic field **B** adjustable in intensity and spatial directions during the printing process [1]. This device is based on the concept of the Halbach array, a specific arrangement of permanent magnets that significantly enhances the magnetic field on one side while virtually nullifying it on the other side [2]. This design allows the generation of a homogenous magnetic fields, whether in dipole, quadrupole, or even higher-order multipole configurations, within the printing region. By incorporating two concentric Halbach arrays in a cylindrical configuration alongside a solenoid, we enable the manipulation of a magnetic microstructure in the three spatial directions, i.e. $\mathbf{B}=(B_x, B_y, B_z)$. This, in turn, facilitates the self-assembly and spatial orientation of magneto-responsive fillers at each stage of the printing process.

After introducing theoretical and technical aspects of the device, several examples will be shown to demonstrate the capabilities of the devise to print magneto-responsive elements with spatially controlled microstructures.

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WAVELENGTH ORTHOGONAL PHOTOCHEMISTRY IN ADDITIVE MANUFACTURING: TOWARDS PHOTOPOLYMERS WITH TAILORED PROPERTIES

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Abstract

Orthogonal photoreactions have gained increased attention in polymer chemistry over the last decade.[1] The selective activation of chromophores with light of different wavelengths enables the spatial and temporal control of the material properties in lithography based additive manufacturing.[2,3,4]

In this contribution, several photo crosslinkable groups were investigated and introduced in thiol-ene reactive systems. The sequence-dependent λ-orthogonality of network formation and crosslinking reaction allows for the spatially resolved alteration of thermo-mechanical properties during or after 3d printing.

Furthermore, the selective activation of bond exchange reactions in photopolymers by sequence-dependent λ-orthogonality was studied.[5] Therefore, a temperature-resistant (> 200 °C) organic phosphate with a photolabile o-nitrobenzyl protecting group was introduced into a visible light-curable thiol-ene resin. Once cured, irradiation at 372 nm spatiotemporally activates the phosphate, which catalyzes transesterifications at elevated temperature. The formed catalyst has no effect on the thermal stability of the polymeric network and allows the activation of bond exchange reactions in selected domains of printed 3D objects.

The use of sequence-dependent λ-orthogonality easily enhances the versatility of lithography-based additive manufacturing and is an important step towards establishing this technology in our daily lives.

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Volumetric 3D Printing of Viscous Photopolymers with Xolography

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Xolography as novel volumetric 3D printing technology rapidly produces objects from subcentimeter scale up to the size of dental models within a matter of minutes.[1] The technology exploits dual-color photoinitiatiors, which molecularly combine type II photoinitiation motifs with a photoswitching function. This makes the dual-color photoinitiator responsive to light of two differing wavelengths, in a way that light of the first wavelength pre-activates the dormant initiator A, while light of the second wavelength transforms the pre-activated form B into the initiating species C, which induces curing of the photopolymer. Thus, with dual-color photoinitiation the zone of polymerization is restricted to regions, where light of *both* wavelength is present *at the same time*.

In Xolography we intersect a thin UV light sheet plane with a visible light projection within the volume of a photopolymer-containing vat. Only at the intersection points curing of the photopolymer is induced, generating a freely floating object within the resin. The technology fundamentally differs from other layer-based 3D printing methods allowing new perspectives for object design, material selection and fabrication processes[2], e.g. the use of highly viscous resins and the 3D-printing of layer-less objects with isotropic material properties and optical grade surfaces.

In this presentation we will discuss the basic working principles of dual-color photoinitiation and the uniqueness of Xolography in terms of fabrication speed, material selection and its application for optics printing and biofabrication.

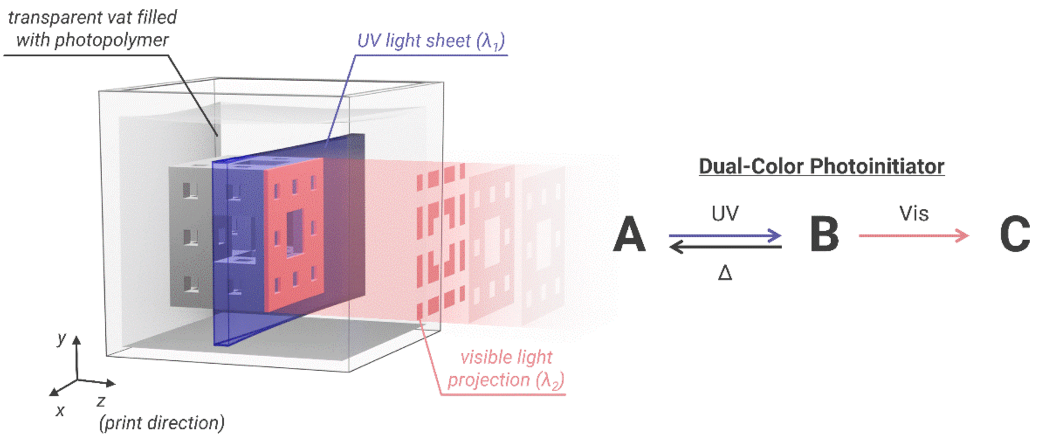

Figure 1. Principles of dual-color photoinitiation and volumetric 3D printing with Xolography.

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DEVELOPMENT OF COMPOSITE PHOTORESISTS FOR 3D AND 4D PRINTING

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The use of 3D/4D printing to create new composites is diversifying applications in fields such as robotics, medicine, etc. The design of this type of material in 3D printing is still limited and does not result in high quality objects[1,2]. In this communication, we introduce a simple route to fabricate composite materials exhibiting dual stimuli. Special attention has been paid to the design of 4D composite in order to bring a fine control to the reversible shape deformation. One of the key parameters lies in the insertion of metallic gold nanoparticles into hydrogel object to confer it a 4D feature[3-4]. Firstly, a description of the synthesis of the nanoparticles followed by the analysis of the morphology/size/dispersion by UV-vis spectrum and TEM imaging are performed. Different concentrations of nanoparticles were used, with the aim of observing its impact on the photoreactivity/viscosity of the formulations and their printability. Resolution and fidelity criteria regarding the CAD model were assessed by investigating printed objects by SEM microscopy. Finally, camera tracking combined with different mathematical models are used to understand the swelling and thermal properties of these objects. By playing with the light intensity or the nanoparticles concentration, the increase of temperature can be controlled in a precise manner leading to the production of a 3D object that responds to a dual stimuli: moisture for swelling and heat for returning the printed object to its initial size (Figure). By taking advantage of the synergy between these dual properties, progress to various fields such as soft robotics can be envisioned.

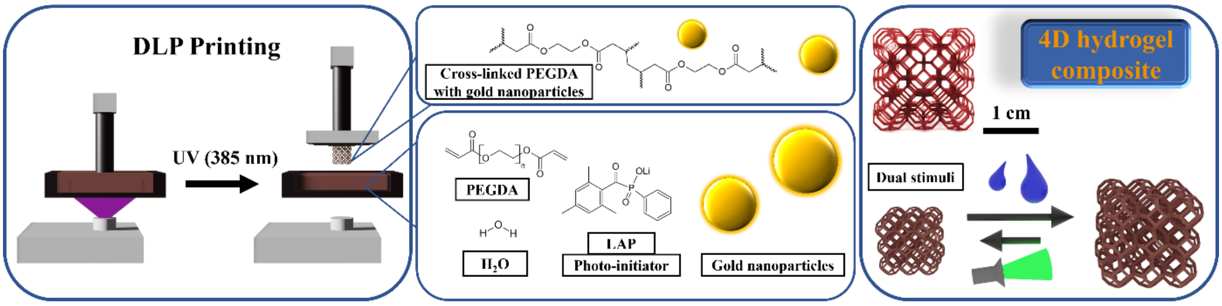

Figure : Global outline of the subject

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PROGRAMMABLE LIQUID CRYSTAL ARCHITECTURES MADE BY 4D MICROPRINTING

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Humankind always sought to create tools which allow the accomplishment of tasks that would be difficult or couldn't be done otherwise. However, reproduction of simple tools at the microscale often require time consuming and multi-steps processes. To respond to increasing needs in healthcare and in manufacturing, nanorobotics has to change paradigm to overcome the current limitations on dexterity, compactness, range, and precision. 4D printing concept appears in 2013 with the idea to facilitate the assembling of macroscopic objects. The fourth dimension refers not only to the ability for material objects to change form after they are produced, but also to their ability to change function after they are printed. At the microscale, 3D direct laser writing (3D DLW) based on multi-photon polymerization has become the gold standard for submicrometer additive manufacturing.[1-2] Various stimuli-responsive materials, especially hydrogels and liquid crystal elastomers (LCEs) have been employed to manufacture advanced microactuators by 3D DLW. In particular, LCEs have attracted considerable attention in the last 5 years due to their reversible, large shape-morphing and their fast response towards temperature or light stimuli. However, their processability by 3D DLW is not easy and the resulting objects rarely exhibit controlled and predictable deformation. The deformation of LCEs microactuators is mainly controlled by the mesogenic alignment design, which should be programmed before photopolymerization. Interestingly, this programming mainly lies in coating industry strategies and is thus not appropriated to 3D microfabrication process. In order to increase the complexity of deformation and thus to fulfil the requirements of nanorobotics, new programming strategies must be implemented in parallel with the development of new photosensitive resins dedicated to 3D DLW.

In this work, we propose a new alternative to perform the alignment of LCEs in a precise manner. By playing both on the orientation strategy and the fabrication parameters, different deformations (curling, bending, twisting…) can be programmed starting from a single CAD model. A collection of building block is first demonstrated, then assembly of these building block is achieved, leading to 3D micro-objects presenting sophisticated behaviour. Finally, the fine control offered by our approach is illustrated by building a micro-actuator and investigating its performance (amplitude, speed of deformation… Fig. 1). This work opens up new prospects for moving from a programmable material to a functional 3D-printed device.

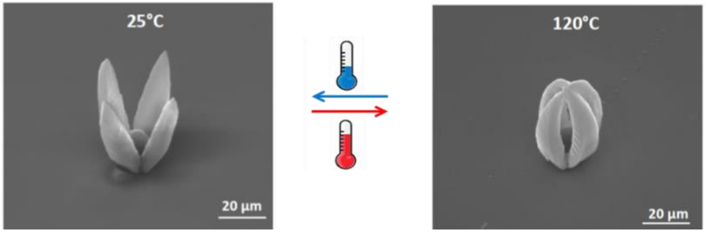

Fig. 1: Thermal actuation of LCE clamp like structure made by 4D microprinting. Case of simple reconfiguration from an open to a close form.

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PROGRAMMABLE ASSEMBLY OF MICROSTRUCTURES MADE BY TWO-PHOTON POLYMERIZATION

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Hierarchical structures in nature have inspired numerous applications in chemistry, biology, optics, and mechanics, as well as in scientific research and technical implementations [1]. Among many microfabrication techniques, two-photon polymerization (TPP) is a well-established method [2] for creating complex 3D micro-objects with stimuli-responsive and reconfigurable surface properties [3,4]. TPP-based laser printing capillary-assisted self-assembly (LPCS) strategy appears as a prime position technique for fabricating periodic structures [5]. However, up to now the controlled assembly of the pillars has uniquely been employed to create homogeneous arrays or simple text made by standalone pillars (see Figure 1-A). In addition, grayscale two-photon lithography (GTPL) has emerged recently as a method for printing programmable objects by tuning the laser power during the printing process [3]. Inspired by the concept of GTPL, the aim of this work is to tailor the mechanical properties of micropillars to obtain heterogeneous structural assembly. Various assemblies of mono- and multi-material acrylate based micropillars with different configurations can be achieved by adjusting the height, arrangement, laser power and printing speed to guide capillary force (see Figure 1-B).

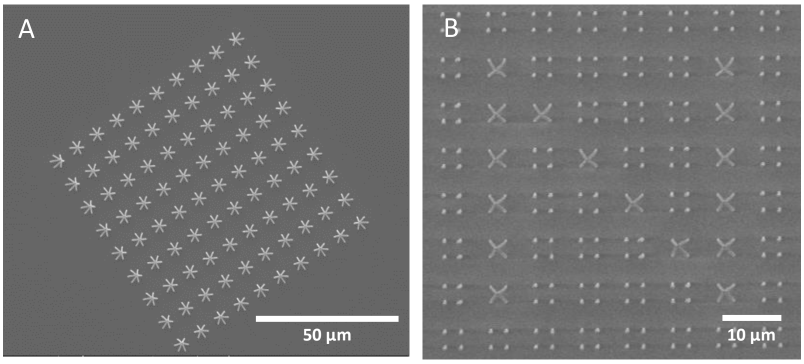

Figure 1: SEM images of micropillars obtained by TPP. (A) Homogeneous capillary self-assembly of pillars in hexagonal arrangement. (B) Heterogeneous structural assembly of micropillars. Letter N inside a CNRS-lettering pillar array.

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SUSTAINABLE EPOXY-METHACRYLATE INTERPENETRATING POLYMER NETWORKS: broadening the scope of high-performance materials for stereolithography

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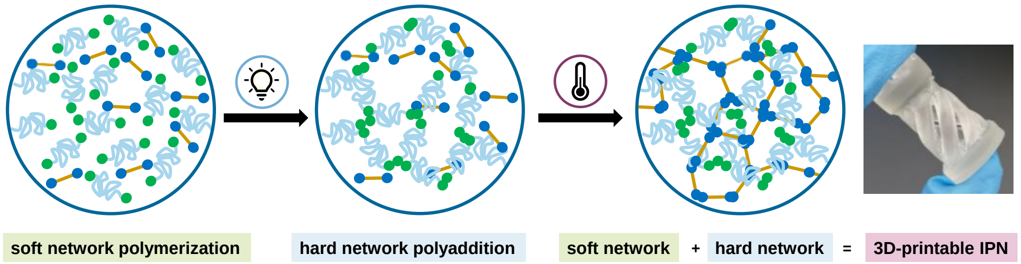
In the last decade, the global market for photopolymerizable resins in lithography-based 3D printing technologies has grown exponentially. Commercially available resins, however, are based on epoxides and (meth)acrylates, generally derived from fossil resources. Next to the predicted scarcity of fossil resources, evermore social emphasis is shifted towards the environmental impact of such materials, as crosslinked petroleum-based polymers bear a large carbon footprint and are inherently non-recyclable or (bio)degradable. Furthermore, the highly crosslinked and inhomogeneous nature of these materials leads to insufficient mechanical properties (e.g. brittleness) and thus, limits their application as high-performance materials. In this study, interpenetrating polymer networks (IPNs) with a high content of renewable carbon were utilized to tackle the abovementioned problems. IPNs were produced using an orthogonal, dual-curing strategy, combining a photopolymerizable high-molecular weight dimethacrylate with epoxy-alcohol polyaddition. While the dimethacrylate delivered an elastic and wide-meshed network, the epoxy-alcohol matrix delivered stiffness and mechanical strength.



Herein, both networks were optimized individually and their (photo-)reactivity and (thermo)mechanical properties were assessed. Combining both networks ultimately led to materials of high T_G (50-54 °C), excellent tensile toughness (13 MJ m^{-3}) and while simultaneously achieving high monomer conversions (over 90%). An in-depth phase analysis *via* AFM was conducted to explore the phase distribution and compatibility of bio-based IPNs. Finally, we could demonstrate the first successful application of bio-based epoxy-alcohol and methacrylate IPNs in lithography-based 3D printing by the fabrication of complex, free-standing and hollow objects. [1]

Acknowledgements
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3D Printing of some unusual monomers

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With the direct 3D printing of cyanate esters via Hot Lithography, without the need of assisting matrix polymers or elaborate functionalization via allyl or epoxy groups, it is possible to freely shape a class of high-performance materials. Until now, they were shaped using time-consuming and expensive molding processes. These are characterized by good mechanical, dielectric and outstanding thermal properties (glass transition temperatures over 300 °C). By developing an initiator system adapted to hot lithography, we were able to directly 3D print structures with good thermo-mechanical properties (Tg above 330°C) for the first time[1].

The 3D printing of phenol-formaldehyde resins (better known as Bakelite) is another milestone. Although this is one of the oldest synthetic thermosets (invented in 1907), it still has enormous importance in industrial applications. This class of material is characterized by its high chemical and thermal resistance and flame-retardant properties. Here, too, the development of a hot lithography-compatible formulation meant that for the first time, the complex and inflexible hot-pressing process for producing Bakelite workpieces could be replaced by a high-resolution 3D printing process[2].

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HIGH PERFORMANCE INTERPENETRATING POLYMER NETWORKS FOR HOT LITHOGRAPHY

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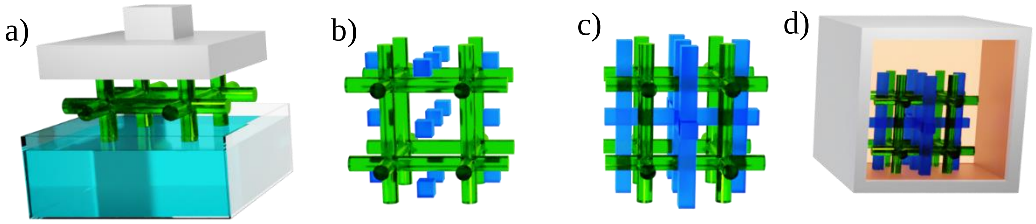
The versatility of lithography-based 3D-printing technologies led to its establishment in today's industry. Complex and highly individualized products are possible, though they also hold some disadvantages. The yielded polymers lack toughness and suffer from overall bad mechanical performance.

We decided to tackle this problem by utilizing an epoxide-alcohol system within a methacrylate matrix. The epoxide-alcohol system provides good mechanical performance, while the methacrylate acts as a scaffold for the 3D-printing process. Combined an IPN is yielded with good printability as well as good mechanical properties like high toughness.

Each network is optimized separately. For the epoxy-alcohol system, the twist is that we have a polyaddition reaction, with low reaction speed but good mechanical properties. These properties are achieved by the high network homogeneity. The low curing speed of the epoxide alcohol system is circumvented by introducing a radical system that acts as a scaffold and enables printing.



a) printing of the soft network b) soft network soaked with uncured hard network c) cured IPN d) post-curing of the IPN to ensure full conversion

The networks were tested with respect to their (thermo)mechanic behaviour. For this purpose, tensile tests as well as DMTA measurements were performed. The polymers that seemed most promising were combined into one IPN and again tested on these properties to yield the best-performing IPN.

For additive manufacturing as a possible application, a dual cure approach was chosen wherein sequential, semi-orthogonal light-curing was applied. This way fast printing can be combined with the slowly curing alcohol epoxide system and its benefits for the mechanical properties.

Acrylate Photopolymers in Additive Manufacturing: A Dive into Thermal Stability and Curing Kinetics

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Additive manufacturing (AM) of plastics stands as a forefront technology in the 21st century, offering exceptional design flexibility and finding applications across diverse industries. Photopolymers, particularly UV-light activated polymers, claimed a significant market share in AM materials in 2021, highlighting their importance. Acrylates, fundamental monomers in photopolymers, enabling rapid processing, intricate geometries with high resolutions, and a broad material spectrum, making them a focal point in various AM technologies. However, these advancements introduce temperature-dependent curing and decomposition behavior of acrylates as significant process-related challenges.

This research delves into a comprehensive analysis of the curing behavior and thermal stability of acrylic photopolymers concerning varying UV-intensities and isothermal temperatures. The study employed thermogravimetric analysis (TGA) with in-situ Fourier-transform infrared spectroscopy (FTIR), and differential scanning calorimetry (DSC) with UV light source (UV-DSC) to scrutinize thermal stability and curing behavior. Characteristic gases evolving at elevated temperatures are identified and their relevance to the curing process is discussed. Calorimetric results showcased that higher UV-intensities significantly augmented the reaction rate, reaching maximum rates before 50% conversion. Isothermal temperatures exhibited a discernible effect on the reaction enthalpy related to both the reaction speed and extent, revealing an accelerating impact up to 90°C. Additionally, the study identified 2-propenoic acid, 2-propenyl ester as a temperature-sensitive and volatile component influencing the curing process. These findings serve as a foundational reference for future investigations, particularly in the comparison of various kinetic curing models.

3D DLP printing of epoxy based materials controlled by the addition of derivate of pyridines

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Additive manufacturing, especially 3D DLP printing, has undergone several technological improvements over the years. However, the photosensitive resins are mostly based on the radical polymerization of acrylate monomers due to a fast reaction and a spatial and temporal control under exposure. Nevertheless, other type of polymerization can be implemented to extend the applications field. The cationic chain polymerisation of epoxy monomers is an interesting alternative. However, the confinement of the reaction is limited due the living characteristic of the active specie. Furthermore, there is a lack of control over the reaction, as the polymerization rate, inhibition and exothermicity depends strongly of the monomer used[1-5].

In order to have a control over theses parameters regardless the structure of the monomer, several retarding agents and inhibitors have been investigated, such as ether crowns[6] and amines[7-10]. Especially, derivate of pyridines enable a various control over the reaction, which help to confine the polymerization and permits printability[11].

In this communication, several derivate of pyridines were investigated in order to adjust the epoxy polymerization kinetic. The reversible addition of the initiating specie H^+ on these compounds ensure the printability of complexes materials due to the significant increase of the reaction confinement. Moreover, several parameters (impact of the inhibition, heat flow, dark polymerization) are discussed to explain the high resolution of the printed material obtained.

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“GREENER” STEREOLITHOGRAPHIC RESIN FROM RECYCLED ALUMINA POWDER

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Today there is a growing interest in the use of ceramic enriched materials to manufacture parts that show all the advantages of ceramic elements, like strong dielectric behaviour, high thermal conductivity and stability, and stiffness. Additive manufacturing techniques can be applied as cost effective fabrication technology to reduce at the same time the manufacturing complexity and wastes production. The development of new 3D printable composite materials is a widespread research topic, and the attention is focused on alumina (Al_2O_3) and/or zirconia (ZrO_2) powders as fillers for photocurable resins. In particular, UV curable resins enriched with Al_2O_3 nano- or micro-particles are of great interest [1], [2], due to their relatively easy preparation processes and their wide range of applications in different fields. Moreover, such alumina-enriched resins can be employed to fabricate complex objects with high-resolution additive manufacturing techniques, e.g. stereolithography (SL) 3D printing [3] as in the present work. This promising advanced technique induces polymerization in a photosensible resin, through UV or near UV lasers, with a tens of µm beam spot, speeding up the production processes of ceramic components. The composition of these resins is commonly based on an acrylate monomer, a photoinitiator, a solvent and a dispersant, used for powder suspension stabilization. Al_2O_3 commercially available powders, specifically tailored for resin preparation, are typically hundreds of nm in diameter [4]. The aim of this work is to prepare a UV curable “green” resin for SL enriched with recycled alumina powders instead of fresh ones. Such powders were recovered from sandblasting machines, in order to achieve a concrete example of circular economy. In this study, 60phr Al_2O_3 microparticles (10µm) were incorporated in a PEGDA based resin, eliminating dispersants to increase the environmental sustainability. The so-prepared resin was tested to verify its printability and stability, proving that alumina particles are temporarily stable in suspension, about 4h, assuring the printability of the resin. The alumina powders and the printed samples were also characterized to prove particle surface composition and morphology, and to confirm Al_2O_3 particles loading. Promising results on the final printed parts pave the way for a new method for alumina waste recovery, giving it a second life.

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NOVEL PHOTOCURABLE RESINS DEDICATED TO OBTAINING POLYMER NANOCOMPOSITES IN 3D-VAT TECHNOLOGIES

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Photoinduced polymerization is a photochemically initiated process utilizing a suitable light source emitting electromagnetic radiation in the ultraviolet (UV) to visible (VIS) range. Photopolymerization processes are now widespread and rapidly developing with technologies related to the molding of three-dimensional models employing light-initiated 3D printing and the printing industry, where they are commonly used for photo-curing UV varnishes and inks. In addition, an interesting application of photoinitiated 3D printing is its implementation for obtaining photo-curable polymer nanocomposites. Composite materials are a class of multifunctional materials that are very popular due to their favorable properties. Particularly worthy of attention are nanocomposite materials, in which the addition of nanofiller changes the final properties of the product, for example: improves its thermomechanical properties, increases its heat resistance, and provides conductive properties. The final properties depend on the selection of a suitable nanofiller, among which carbon nanotubes, silica, aluminum oxides, and natural and polymer fibers are widely used additives.

The present work concerns the study of pentafluorostilbene derivatives. We investigated the suitability of 10 1,2,3,4,5-pentafluoro-6-[(E)-styryl]benzene derivatives to behave as potential photosensitizers of the diphenyliodonium salt IOD to initiate radical, cationic, and hybrid photopolymerization processes applying light sources in the ultraviolet and visible range. The next step was to verify the possibility of obtaining photo-curable polymer nanocomposites using 3D printing technology.

The presented pentafluorostilbene derivatives demonstrate favourable absorption properties, especially in visible light, absorbed up to ~420-450 nm. Spectroscopic properties investigations of stilbene derivatives have shown that their absorption characteristics are compatible with the emission characteristics of light sources applied in DLP printers ($\lambda = 405$ nm). The examined compounds have very beneficial redox properties, which allows their use in two-component systems photoinitiating with iodonium salt to initiate radical, cationic, and hybrid photopolymerization utilizing a light source from both ultraviolet and visible range. According to a variety of spectroscopic, electrochemical, as well as kinetic studies, the most effective initiator system (M10+IOD) was selected, which in a further stage of research was employed for application research related to the preparation of photo-curable polymer nanocomposites using 3D-VAT technology. The high photoactivity of the M10+IOD system allowed its application as an efficient photoinitiating system for 3D-VAT printing of ZnO-nanocomposites using DLP technology.

Acknowledgments

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Enhancing Photopolymer Performance: Exploring Phase Separation in (Meth)acrylate Systems for Additive Manufacturing

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Photopolymerization-induced phase separation presents a promising approach to enhance photopolymer performance for additive manufacturing (AM)-related applications such as biomedical engineering, tissue engineering, and digital dentistry. This phenomenon occurs in multicomponent systems with marginal incompatibilities including various monomers, oligomers, and reactive diluents at the nano to microscale levels.

The study explores a phase-separable system characterized by significant transparency changes after UV light radiation. The system comprises isobornyl Acrylate (IBOA) diluted aliphatic urethane diacrylate oligomer (UDA) and bisphenol-A-ethoxylate di-methacrylate monomers (Bis-EMA) photopolymerized by the activation of Diphenyl (2,4,6-trimethylbenzoyl) phosphinoxid (TPO) as the initiator agent.

Tensile strength, impact resistance, and thermal stability were among the qualities that were quantified before and after the system was treated to 20 wt. percent 4-Acryloylmorpholin (ACMO; Sigma-Aldrich), a highly polar reactive diluent. Optical properties such as phase separation onset, duration, and final transparency were assessed using a bespoke developed setup.

The research also explores the capabilities of atomic force microscopy (AFM) in characterizing photopolymers from fracture mechanics and microstructure-property points of view. Special focus was therefore given to the effect of sample preparation on a consistent, accurate and reliable AFM measurement. Furthermore, to obtain a homogeneous fracture surface with minimal effects of irradiation intensity throughout the component's thickness, the AM process Hot Lithography was employed. The results demonstrated the high capability of this technique in processing highly viscous formulations which is advantageous in preparing 3D-printable photopolymers with improved toughness.

Keywords: Photopolymerization, Phase Separation, (Meth)acrylate resins, Atomic Force Microscopy, Hot lithography

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DIRECT 3D PRINTING OF POLYESTER AND POLYCARBONATE NETWORKS

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Polyesters and polycarbonates are versatile (bio)degradable materials, which are particularly interesting for biomedical applications. Therefore, their manufacturing via stereolithographic methods such as laser- or digital light printing stereolithography is highly desirable for the customized fabrication of degradable biomedical devices.

However, traditional stereolithographic processes are highly dependent on the reactivity and viscosity of photosensitive resins, particularly when printing macroscopic constructs. Therefore, typically utilized photopolymerization methods rely on radical photopolymerization. While mixed photopolymerization via radical and cationic mechanisms became available a while ago via photoacid generators, which form radical cation intermediates and subsequently cations upon irradiation, 3D printing via purely cationic photopolymerization remained elusive until recently. Now, pure epoxide resins can be printed via cationic ring-opening polymerization in stereolithography. However, ring-opening polymerizations are dependent on ring strain and prone to side reactions, limiting their reactivity drastically compared to radical photopolymerization.

This is particularly limiting when polymerizing larger rings with more versatile functionality, such as lactones, cyclic carbonates, spiro-orthoesters or spiro-orthocarbonates. With the rise of hot lithography, such monomers become printable for the first time due to increased reactivity at elevated temperatures. We have demonstrated 3D printing of pure polyesters[1-2] and polycarbonates[3] via ionic ring-opening polymerization. In-depth photopolymerization analysis has elucidated the pathways of ionic polymerization reactions at high temperatures. Bulk photopolymeric specimens of different compositions have been analysed with respect to their thermomechanical properties, revealing easy tuneability within a wide range of mechanical properties. Furthermore, volumetric shrinkage of bulk specimens was eliminated entirely through double ring-opening photopolymerization of spiro-monomers. Finally, successful 3D printing via cationic photopolymerization has been demonstrated.

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A new generation of organic semiconductors for 3D printing

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Since the initial report of the conductivity of conjugated polymers (CP) in 1977, the enthusiasm for developing their use in optoelectronic devices has continuously grown up [1]. Indeed, organic semiconductors possess many advantages over other semiconductive materials as their properties can be finely tuned thanks to chemical engineering, and they can be easily physically manipulated with cheap techniques [2]. CP possess potential applicability in emerging fields like plasmonics, nanophotonics and bioelectronics [3]. However, most of them are usually processed from solution which leads to the fabrication of materials with limited shapes. Furthermore, with the continuous miniaturization sought in electronic components, the semiconductors have to be processed with smaller and smaller features. Along these lines, research has been driven towards evaluating new technologies. Among different techniques, Vat photopolymerization 3D printing, based on radical polymerization stands out since it can achieve microscale features. However, the development of this technique is strongly hindered by the limited availability of suitable photoresins.

In view of filling this gap, we will present our work on the development of solvent-free resins for the fabrication of a new generation of microscale organic semiconductors. After proving the success of modifying the starting precursor, the reactivity of the photocurable formulations was investigated both at the macro (moulding) and micro (3D printing) scale. Subsequently, the thermal properties of the macro samples were investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) respectively. After optimizing the printing parameters, the morphology and the fidelity of the 3D printed micro samples to the digital model were carefully evaluated by scanning electron microscopy (SEM). Finally, the electrical measurements performed on both the macro and micro samples will be discussed. These promising results may envisage the potential application of these 3D printable materials in microelectronics.

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SELF-HEALING HYDROGELS PRINTED BY PHOTOINDUCED 3D PRINTING TECHNIQUES FOR BIOMEDICAL APPLICATIONS

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Self-healing hydrogels (SHHs) are becoming increasingly important in biomedicine because of their similarity to biological tissues and their ability to recover from damage. Because of these characteristics, SHHs can serve as ideal 3D scaffolds for regenerative medicine [1]. So far, such hydrogels have been processed mainly via extrusion-based technologies, limited in design and resolution [2]. In order to obtain more complex objects with better resolution, in this study light-induced 3D-printing (Digital Light Processing – DLP) technique has been exploited. This research work deals with the development of a biocompatible, self-healable and photo-reactive hydrogel, able to be 3D printed through DLP. The printed structures were characterized mechanically and chemically, to find possible application in cartilage tissue engineering. A commercial DLP printer and water-soluble, commercially available materials were used to fabricate the hydrogel. In particular, thiol-ene polymerization has been exploited in the printing process, while boronate-ester bond chemistry plays a role in self-healing ability. The printing process was optimized by adding a natural radical scavenger based on tannic acid. In such conditions, complex 3D objects containing up to 85% water were printed (Fig. 1). The ability to self-repair was evaluated by cutting the 3D printed specimens and bringing the two ends together: after 48h, the specimen is capable of self-standing, while after 72h, it withstands up to 75% elongation (Fig. 2). Up to 3 cycles of breaking and self-healing on the same specimen have been performed, although the maximum elongation is reduced to about 20%. The resulting hydrogel was characterized in terms of NMR spectra, rheological properties, swelling abilities, resistance in aqueous environments, tensile and compression characteristics. Finally, biocompatibility and cytocompatibility tests will be performed to verify applicability in tissue engineering.

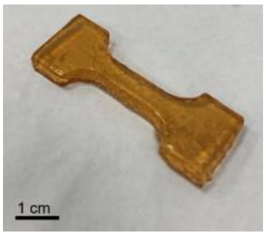

Fig. 1. *3D printed structure*

Fig. 2. *Self-healing ability after 72h at room temperature*

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Use of boronic-azodye towards 3D printing self-healing hydrogel

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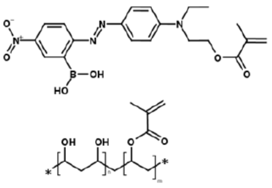
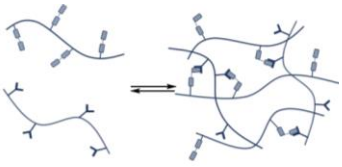
In the biomedical field a very active branch of research concerns the development of functional hydrogels. When composition and morphology of hydrogels are appropriately designed, they can find various applications, especially in the field of tissue engineering. Above all, synthetic and/or natural hydrogels are used as artificial systems capable of replacing or promoting the regeneration of damaged tissues. So far, this type of hydrogel has been processed by conventional methods; however, those approaches are not able to reproduce the complex inner structure and some properties of tissues like self-healing capabilities. Herein, we present a light- regulated self-healing hydrogel processable through 3D printing by using a commercial Digital Light Processing (DLP) printer.

A dye based on azobenzene was employed. Azo dyes can undergo cis-trans configurational changes when irradiated at a specific wavelength. Additionally, azobenzene was modified with attached boronic acid groups; these functional groups can form dynamic covalent boronate ester bonds with a diol [1]. As for the polyol, hydrated polyvinyl alcohol (PVA) methacrylate has been used because, as reported in the literature, it is the most suitable for forming polymer networks by reacting with boronic acid through boronate ester bonds [2].

The hydrogels were first characterized in terms of printanbility through rheology testing, then the mechanical properties were tested throw dynamic mechanical analysis and sweeling test, in order to verify the compatibility of the hydrogel with human tissues. Finally, a protocol has been developed to verify the self-healing capabilities.

The proposed approach enables 3D printing of hydrogels objects with complex architecture, with mechanical properties similar to human tissues and with self-healing capabilities.





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ADVANCES ON THE PHOTO-CURING OF THIOL-EPOXY RESINS FOR 3D PRINTING

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Thiol-based click resins have garnered significant popularity due to their high reactivity, enabling swift photocuring under mild conditions. Click processes obviate the need for solvents and it importantly avoids the generation of by-products. Thiols have discovered utility within a variety of photo-curable systems featuring allyl or ethynyl-based resins[1-3]. Carioscia and co-workers demonstrated the light-triggered curing of diglycidyl ether of bisphenol A and thiols, which makes this class of reactions interesting for vat photopolymerization 3D printing[4]. However, the resins suffer from high viscosity at room temperature, which makes 3D printing challenging. Jian et al. reported on the low shelf life of these resins, which can cause further problems during 3D printing[5]. In contrast, Bouzrati-Zerelli and co-workers studied the photo-reaction between a thiol and a cycloaliphatic epoxy monomer, showing a slow cure rate and an unsatisfactory conversion, rendering it unsuitable for additive technologies[6]. The current study endeavours to surmount the challenge of formulating a light-curable thiol-epoxy system processable via vat photopolymerization 3D printing. The attainment of this objective necessitates the prepared resin's stability at the printing temperature, its expeditious reactivity upon exposure to light, and its requisite viscosity. To achieve this, a suitable epoxy monomer, thiol crosslinker, photolatent base and sensitizer were selected. The effect of the concentration of the components of the mixture on the photo-curing kinetics and printability was studied. With a selected formulation, 3D printed parts were fabricated and their mechanical properties were determined.

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ESPERANTO
Enhancing the Sustainability of PhotopolymERs ANd phoToinduced prOcesses

Funded by the European Union

3D PRINTING OF MOLECULARLY IMPRINTED POLYMERS BY DIGITAL LIGHT PROCESSING FOR ANTIBIOTICS RECOVERY

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Molecularly Imprinted Polymers (MIPs) as artificial receptors have received considerable scientific attention in the past few decades, as material for biomimetic molecular recognition [1]. The preparation of an imprinted polymer involves the complexation, through covalent or non-covalent interactions, between a template molecule and a functional monomer, followed by polymerization in the presence of an excess of a crosslinking agent. The removal of the template from the resulting matrix leaves behind imprinted cavities, complementary at the atomic scale to the template molecules, thanks to the binding sites exhibited by the functional monomer. MIPs are nowadays employed in a large number of applications and fabricated in a variety of techniques, including photopolymerization methods [2], even though fabrication through additive manufacturing (AM) appears mostly as an unexplored field. The challenge of this work is in the employment of AM technology to realize 3D-printed MIP-based objects. A new composite photocurable resin was developed to be suitable for a Digital Light Processing (DLP) printer, and optimized in order to reach reproducibility. The resin includes Oxytetracycline (OTC, a broad-spectrum antibiotic) as the template molecule, methacrylic acid (MAA) as the functional monomer, Dipropylene Glycol Diacrylate (DPGDA) as the photopolymerizable crosslinker and Dimethyl sulfoxide (DMSO) as the solvent. The interaction mechanism between the carboxylic group of MAA and the hydroxyl and amide groups of OTC was computationally investigated through density functional theory (DFT) calculations [3], including the presence of DMSO.

Different geometries were printed and tested, starting from multi-material disks consisting of a MIP 50 µm thick layer on a 500 µm thick support base of DPGDA. The thickness of the MIP layer was minimized to mimic a functionalization layer on a surface. Then, complex 3D filters were printed, entirely made of MIP resin (Figures (a) and (b)). Lastly, some porous samples were printed, thanks to the addition of salt in the resin, in order to increase the surface area (Figure (c)). The samples were tested for OTC recovery from aqueous media, and the target adsorption was characterized by UV-Vis spectrophotometry.

In this work, DLP was employed to fabricate microstructured samples suited to characterize the material and investigate its capability in target recovery. Nonetheless, the described approach may be applied to develop a resin printable with a higher resolution technique, namely Two-Photon Polymerization, to obtain the patterning of MIPs at the nanoscale and the integration of MIPs in micro and nanosystems.

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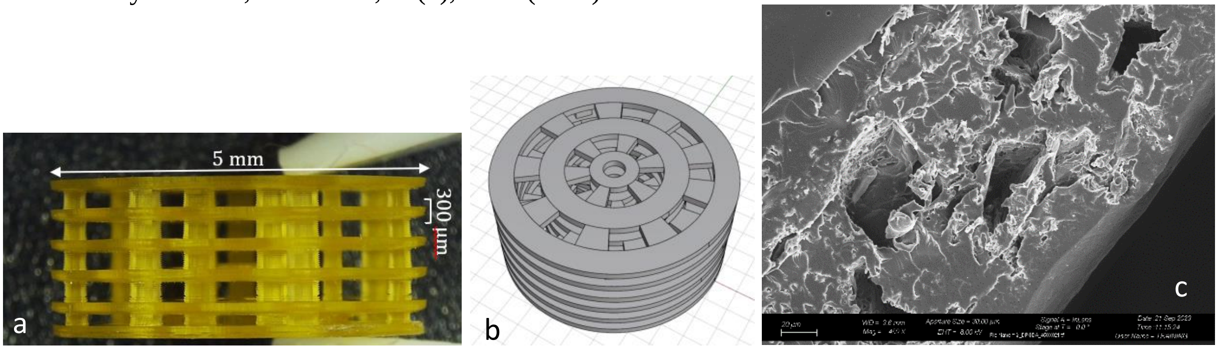

Figures: (a) Side view picture of the printed MIP filter, and (b) the perspective view of the CAD drawing. (c) SAM image of the cross-section of a porous MIP sample.

Soft Microstructures via Direct Laser Writing

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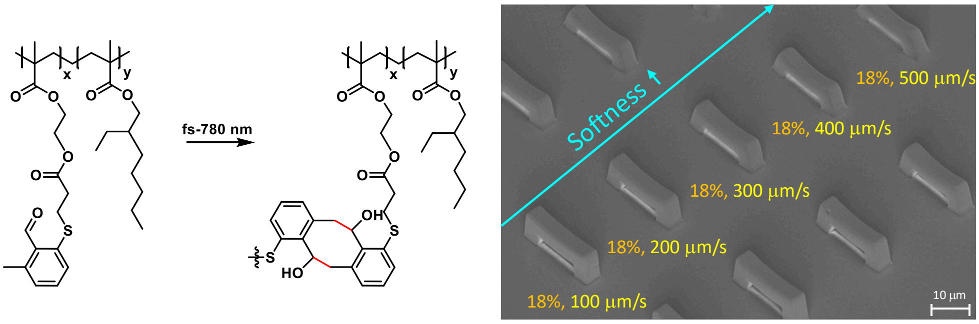
Herein, an additive- and photoinitiator-free photoresist formulation is introduced to fabricate three-dimensional (3D) soft microstructures via the self-dimerization reaction of visible light active *o*-methyl benzaldehydes bound to a polymeric backbone, employing commercially available direct laser writing (DLW) technology based on a 780 nm fs-laser. The photoresist consists solely of a methacrylate copolymer carrying *o*-methyl benzaldehyde (*o*-MBA) thioether units. The mechanical properties measured for the 3D microstructures exhibit similar softness compared to the commercial IP-PDMS resist, with a Young's modulus ranging from 15 to 20 MPa [1]. The 3D microstructures are characterized via scanning electron microscopy (SEM). Our initial experiments indicate that the mechanical properties of the 3D structures can be vastly altered by varying the writing parameters within the writing window. This trend suggests the potential for achieving multi-material properties from a single resist by finely tuning the mechanical properties through careful adjustment of the writing parameters (i.e., laser power, scan speed).



Scheme 1. A polymer network is generated based on the self-dimerization of *o*-MBA thioether units using DLW. SEM images of the 3D microstructures visually demonstrate the gradual alteration in mechanical properties resulting from variations in the writing parameters (laser power:18% (laser power @100% ≈ 50 mW), scan speed range: 100-500 µm/s).

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CERAMIC BONE SCAFFOLDS BASED ON ZIRCONIUM OXIDE NANOPARTICLES PREPARED USING PHOTOCHEMICALLY INITIATED 3D PRINTING

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Photochemistry and consequently radiation-initiated polymerization processes play an extremely important role in materials engineering. Photopolymerization processes are widely used in many industries including biomedical engineering, automotive and dentistry. These processes are currently rapidly expanding with technologies related to forming 3D models using light-initiated 3D printing. One more interesting application of photoinitiated 3D printing is its deployment for obtaining photo-curable polymer nanocomposites.

Additive manufacturing of polymers with nanoparticles using Digital Light Processing (DLP) is a relatively new area of research that has attracted significant attention in recent years. This technique offers high resolution, speed, and accuracy, making it an attractive option for various applications including biomedical engineering. Using this technique, the liquid resin can be easily mixed with a variety of nanofillers for the manufacture of functional nanocomposite materials. Nanofillers incorporation in a polymer matrix can improve the mechanical and thermal properties of the final material.

The application of three-dimensional printed polymer scaffolds in repairing bone defects is a promising strategy. Zirconium dioxide (ZrO_2) nanopowder can enhance the hydrophilicity of polymer materials. At the same time, the elastic modulus of ZrO_2 is matched with human bones, has high mechanical strength and fracture toughness has excellent osteointegration, and can be combined with living bone. The good hydrophilicity of nano-zirconia particles can improve the biocompatibility of composite materials. The good mechanical properties of the zirconia material are used to improve the mechanical properties of the composite material so that the composite material can meet the mechanical properties required by the bone scaffold. Finally, combined with 3D printing, a composite scaffold with a regular grid structure was constructed to be used in bone tissue engineering repair.

The suggested bio-inspired ceramic bone scaffolds have enormous potential for applications in bone tissue engineering and regenerative medicine. The combination of 3D printing technology and zirconium oxide nanoparticles offers a promising route to producing patient-specific scaffolds with enhanced biological functionality and improved mechanical properties. This nanocomposite could serve as a potential candidate to be used for bone tissue engineering. The 3D scaffolds were printed utilizing DLP technology (Lumen X, Cellink). For analysis of microstructure, phase composition, and mechanical properties of printed scaffolds, the following research techniques were applied: scanning electron microscopy (SEM), thermogravimetric analysis (TGA), and mechanical tests.

Acknowledgments

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INVESTIGATION OF THE EFFICIENCY OF FREE-RADICAL AND CATONIC PHOTOINITIATORS DURING VAY PHOTOPOLYMERIZATION OF IONOGELS USING 3D PRINTING TECHNOLOGY

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Light-initiated polymerization processes are now conquering the chemical market and are used in many fields. Moreover, safe light sources such as UV-LEDs and Vis-LEDs are extending the function of these processes to medicine and dentistry. Polymerization processes based on photochemical phenomena have several advantages: significant reaction kinetics, no need for high-temperature processing, low energy consumption, and no solvents.

Recent years have shown a strong interest in polymerization carried out in ionic liquids (ILs). The first reason for this development is usually the need for *'green solvents'* to replace volatile organic compounds[1]. However, studies have shown that this is not the only reason for the development of polymerization in ionic liquids. In fact, most polymerizations carried out in ILs show an increase in polymerization rate and polymer chain length compared to polymerisation in classical organic solvents. Ionic liquids can also act as plasticizers, stabilizers, modifiers, etc., and polymer gel electrolytes can be produced by thermal polymerization of monomers in ionic liquids, leading to the formation of composite conducting materials.[2]

In the present study, the efficiency of initiation of photopolymerization in ionic liquids (ILs) by selected cationic and radical photoinitiators was investigated. Spectroscopic measurements of both the initiators used and the ionic liquids studied were carried out. The spectroscopic studies carried out included absorbance studies, photolysis of the ionic liquids and initiators, and photolysis of systems containing both the ionic liquid and the initiator. In addition, photopolymerization processes were monitored by photo-DSC and real-time FT-IR.

Practical aspects of the application of photopolymerization in ionic liquids were the reason for undertaking research into the effect of ionic liquids on the initiating ability of selected photoinitiators. Ionic liquids have been shown to affect the performance of these photoinitiators. The behaviour, and relative reactivity, of initiators varies depending on the nature of the ionic liquid. The results obtained indicate that special attention must be paid to the choice of photoinitiator when polymerization is carried out in an ionic liquid. Each formulation should have an individually selected photoinitiator.[3]

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COARSE-GRAINED MODELS FOR FRONTAL PHOTOPOLYMERISATION FOR NON-PLANAR MATERIAL ASSEMBLY

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We introduce a series of coarse-grained models for frontal photo-polymerisation (FPP), with varying degrees of complexity, seeking to describe material fabrication by FPP for a wide range of chemistry and process parameters. FPP is a light-driven directional solidification process which yields conversion profiles that propagate in time, in the form of travelling waves, generally under conditions of strong light attenuation and limited mass transfer. Under certain conditions, the travelling conversion profiles are time-invariant, while in general these evolve with time due to a complex interplay of mass or heat diffusion, and polymer network properties. In the simplest form, our models comprise a single equation of motion for a (scalar) conversion fraction φ and a generalised Beer-Lambert law accounting for the spatio-temporal evolution in conversion [1, 2, 3]. The non-trivial coupling of these equations can describe a range of systems, but higher order chemical conversion schemes are needed to account for experimental observations of solidification kinetics, light attenuation and spatio-temporal monomer-to-polymer conversion, acquired by profilometry, AFM and spectroscopic imaging. Our framework provides a range of simple descriptive models, with a small number of system parameters, yet providing a predictive ability for ubiquitous solidification and patterning processes, including 3D printing and non-planar assembly of materials generated via photopolymerisation.

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PHOTOINITIATOR-FREE, ALGINATE-BASED UV COATING

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The increasing number of research studies devoted to the development of bio-based materials reveals their great ability to substitute petrochemical–based materials. Coatings are one of the main applications concerned by this interest. Developing new synthetic routes combining bio-based building blocks and environmentally–friendly processes such as UV irradiation is a very promising emerging field of research. In this study, we present a new approach for the synthesis of bio-based alginate derivatives for photopolymerization without the use of traditional photoinitiators. Their potential adverse effects on human health and the impact on the environment are avoided thanks to this original approach. Alginate, a biopolymer derived from seaweed, is chosen as the primary material for its biocompatibility and sustainability. They are functionalized by vinyl ether or maleimide. Their photocopolymerization without any photoinitiator will be presented (Figure 1). The photocopolymerization step employs maleimide and vinyl ether as a key component of the electron acceptor donor mechanism.

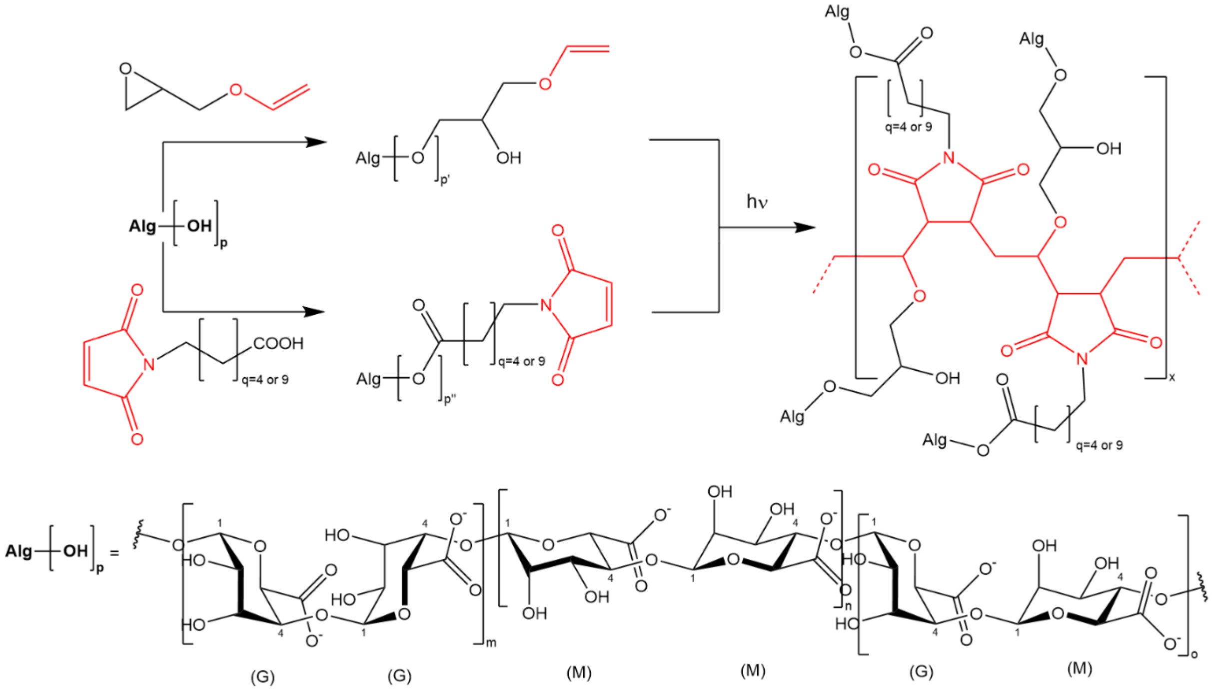

Figure 1. Alginate derivatization and photocopolymerization with vinyl ether and maleimide

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3D printing materials based on anionic photopolymerisation processes

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3D printing is an emerging technique in scientific, industrial and commercial areas, expected to revolutionise our day-to-day lives. Photo-induced polymerisation techniques are well recognised within 3D printing for their speed and precision in addition to their low energy and solvent consumption [1]. The traditionally used (meth)acrylate resins for radical photopolymerisation show drawbacks associated with shrinkage during polymerisation, toxicity in uncured state and inhibition by oxygen [2]. Therefore, there is plenty of room for the development of novel light-sensitive materials for 3D Printing [3]. Anionic photopolymerisation can help to achieve novel functional materials opening up the way to overcome the limitations of radical photopolymerisation. Upon exposure to UV or visible light photolatent base generators (PBG) are able to release reactive bases initiating anionic polymerisation reactions. Such reactions among others are ring-opening polymerisation (ROP) of epoxides, polyurethane catalysis and thiol click reactions involving thiol-ether and thiourethane systems as well as Michael addition reactions [1]. These reactions can open up opportunities for creating bio-based, biodegradable polymers along with materials with dynamic covalent bonds (DCB) capable of being repaired and reprocessed [4].

The aim of this work is to develop new polymeric materials and formulations for PBG-initiated anionic photopolymerization by LED light for 3D printing. Apart from the protocol of formulation, the development process involves the characterisation of the new photocured materials and 3D printed objects together with the optimisation of the 3D printing process. The overarching goal is to obtain a new system with better functionalities and sustainability than the current benchmark. To achieve this bio-based monomers would be used for the creation of biodegradable polymer chains by ROP and for the development of covalent adaptable networks (CANs). The research is aimed to provide in-depth knowledge about the formulation, and properties of materials created by anionic photopolymerisation and their use in 3D printing. The anticipated new material is foreseen to help light-based 3D printing become a more environment and customer-friendly manufacturing method.

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ESPERANTO
Enhancing the Sustainability of PhotopolymERs ANd phoToinduced prOcesses

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Synthesis of Photobase LED Sensitive Photoinitiators

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In recent decades, photopolymerization has undergone substantial progress, evolving into a prominent process across academic and industrial sectors. Its versatile applications span various fields, such as coatings, medical applications, additive manufacturing etc, establishing its widespread utilization. Extensively studied photochemical methods generating free radicals and acids are widely utilized for long time in photopolymerization [1]. Investigations into new polymerization pathways utilizing photobase generators aim to broaden the scope of materials in the field. Though it contends with various issues like oxygen inhibition, migration, and yellowing, the advantages of photobase generators (PBG) make them an appealing substitute. PBG systems offer a novel approach to catalyze a range of reactions, including thiol-Michael, thiol-isocyanate, epoxy polymerization, thiol-thiol, and ring-opening polymerization reactions [2]. The desirable features offered by visible-light activated PBGs include reduced scattering, increased penetration depth, greater functional group tolerance, biocompatibility, high pKa for the released base and potential for wavelength selective multimaterial fabrication. These aspects have inspired the design and utility of novel PBGs in polymer synthesis [3], [4], [5].

This work aims to devise LED-sensitive photobase (PBG) generators, this involves a synthesis process and subsequent characterization to evaluate their potential for application in additive manufacturing. Expected outcomes encompass well-established protocols detailing the synthesis of PBG, along with comprehensive investigations into its photochemical properties under LED irradiation. Sustainability metrics will be established to assess the environmental impact of the synthesized photoinitiators, concurrently fostering expertise in the synthesis and characterization of innovative ionic photoinitiators. This research not only contributes to the advancement of LED-sensitive photoinitiators but also cultivates a deeper understanding of their applicability in additive manufacturing processes, envisaging a pathway towards more sustainable and efficient photopolymerization techniques.

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Two-Photon Laser Printing of RGB Emissive 3D Microstructures

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Light-based 3D printing technologies offer unique opportunities for the creation of highly customized, complex, and functional objects with greater efficiency and precision than traditional manufacturing methods.[1] Although luminescent materials have been widely applied in applications such as sensors, anti-counterfeiting devices or biomedicines, their use in 3D microfabrication, especially in high resolution two-photon laser printing (2PLP), is still limited. In a first work, we explored the use of a new type of fluorophores, which are based on a twisted tetraazaperylene core, for creating emissive organic 3D microstructures. In particular, it was found that the presence of the fluorophore derivatives did not significantly inhibit the photopolymerization process and complex 3D fluorescent microstructures were successfully printed (Figure 1).[2] Recently, the properties of the emitter have been further customized to optimize it for two-photon laser printing, by introducing acrylate groups. This leads to a covalent incorporation of the emitter into the polymer matrix, allowing to accurately tune the concentration and therefore the brightness of the emitter in the 3D printed structures. Further, multi-material prints were conducted with up to four different formulations, containing a red, green, blue, or no emitter to show possible application in ultra-high-resolution displays or anti-counterfeiting.

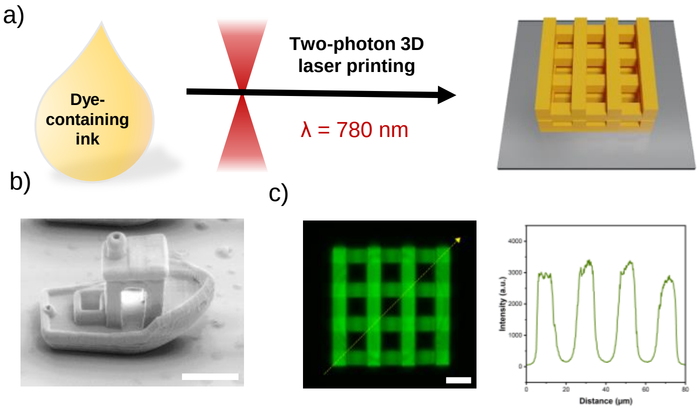

Figure 1: a) Schematic representation of two-photon laser printing using tetraazaperylene-containing inks; b) SEM image of an exemplary 3D printed microstructure, i.e., benchy; c) Confocal microcopy image and profile of a 3D printed woodpile microstructure. Scale bars = 10 µm.

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Volumetric Printing of Hydrogels and Biopolymers using Xolography

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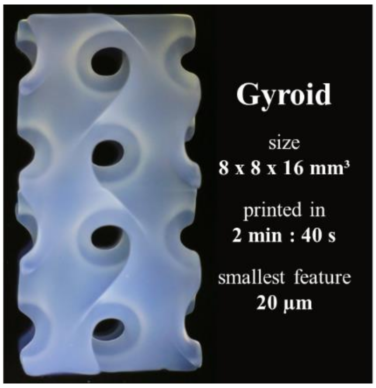
Xolography is a volumetric 3D printing technology that rapidly produces objects from a wide range of photopolymers. Using innovative dual-color photoinitiators, the temporal intersection of ultraviolet and a visible light beam within a resin vat triggers spatially localized polymerization.[1]

This poster showcases the evolution of the technology to volumetric printing in *water-based media*, i.e. the fast and precise 3D printing of synthetic hydrogels and biopolymers. Compared to other 3D printing methods, Xolography's layer-less fabrication process opens new possibilities in object design and engineering of (bio)material properties. For instance, the volumetric nature of Xolography allows processing of soft materials without the need to move them or to exert stress on them during printing. This allows for customizing material properties for specific applications, like tissue constructs, instead of conforming to process requirements such as low viscosity. Further, the process boasts a high fabrication speed in the mL/min range, coupled with a fine feature resolution in the low two-digit µm range. The resulting surfaces are smooth, eliminating the traditional staircase effect.

Xolography allows the creation of superior 3D-shaped hydrogel and biopolymer constructs, holding significance for both fundamental material science and biotechnological applications.



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Direct 3D Printing of Smooth Optical Elements

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Among the various techniques in the field of additive manufacturing, the highest resolution is achieved by photopolymerization based approaches. The most used techniques are layer-by-layer based such as SLA (stereolithography) or DLP (digital light processing). The photopolymerization of one layer after the other causes interfaces between these layers due to different degrees of polymerization resulting in anisotropic objects. Furthermore, the stepwise printing process causes steps on the surface. Consequently, for 3D-printing of optical elements, another approach is required, such as volumetric printing where the polymerization is induced inside of a volume of monomer. While the well-known Two-Photon-Polymerization has low build rate and requires a pulsed laser source of high intensity, dual color volumetric printing (xolography) is presented as an alternative.

A specifically developed photoswitchable photoinitiator is pre-activated with light of a first wavelength and initiates upon subsequent absorption of light of a second wavelength. In such an approach every voxel within a monomer volume can be individually polymerized at the intersection of the light of both wavelengths. The first wavelength (UV) is provided in the form of a light sheet which is moved through a cuvette, while a movie is projected onto the light sheet. This fast and continuous printing process results in isotropic objects due to the absence of layer-layer interfaces. Moreover, smooth surfaces are directly obtained after post-curing without any further treatment such as coatings.

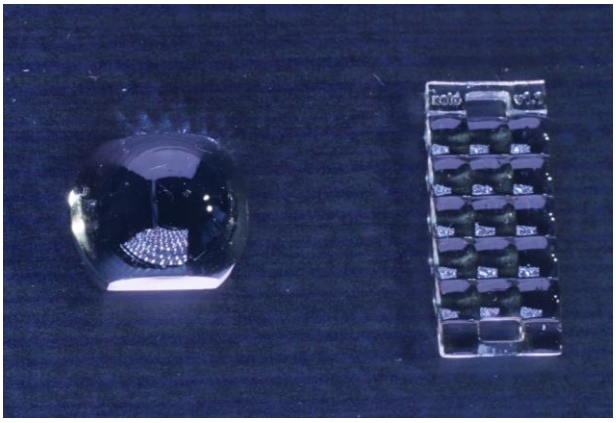

Figure 1. Optical elements printed with Xolography.

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Photoinitiators as Reducing Agents

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In the recent time photoinitiators have found use as (chemically) photo-reducing agents.

In my contribution I will illustrate the "history" of these applications and report on mechanistic aspects and applications.

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Relation between photochemical properties of oxime esters and their efficiency as photoinitiators for free radical induced photopolymerization

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In recent years, oxime esters are of growing interest as Type I photoiniators thanks to their high efficiency in radical photopolymerization. Several structures have been proposed by varying the chromophoric group or the oxime ester substituent in order to improve the initiation properties.

In this paper, the relation between the structure, photophysical and photochemical properties, reactivity, and efficiency in photopolymerizeation processes of four commercial oxime esters has been studied. Their absorption properties were investigated using UV-Vis spectroscopy and fluorimetry. They were correlated to the molecule structures and electronic transitions thanks to density functional theory (DFT) calculations. The understanding of the reaction pathway was supported by photolysis experiments. Finally, photoinitiator efficiency was studied in photopolymerization by real time Fourier transform infrared (RT-FTIR) experiments and the results were related to the photochemical properties.

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Pre-associated ion-pair photoinitiating system for free radical photopolymerization

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A highly efficient photoinitiating system for radical photopolymerization based on a cationic dye having a sub-nanosecond excited state lifetime is presented. The use of an anionic coinitiator allows to override the diffusion limitation encountered for bicomponent systems with short-lived excited state lifetime of the dye[1]. The mechanism of this photoiniating system is described and modelled in order to calculate the dye-coinitiator pre-association efficiency. This factor is showed to rule the observed polymerization rate measured in real-time Fourier transform infrared spectroscopy. Using this photoinitiating system, high reactivity and material curing were achieved even under mild conditions (low photosensitizer concentrations, low LED intensity).

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Speaker's biography:

Léo Niederst has graduated from the ECPM engineering school (Strasbourg, France) and is currently a PhD student under the supervision of Xavier Allonas and Christian Ley, at the LPIM (Mulhouse). Léo is studying the photochemistry of photoinitiating systems for polymerisation.

ONE-STEP SYNTHESIS OF METAL-POLYMER NANOCOMPOSITES BY SIMULTANEOUS PHOTOCHEMICAL POLYMERIZATION AND METAL REDUCTION

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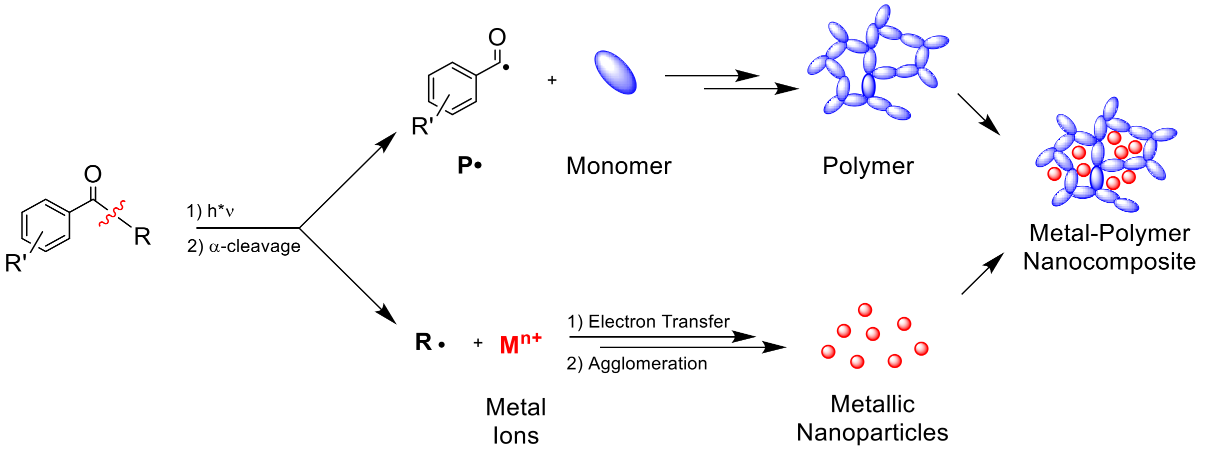
The combination of photochemical metal reduction and photo-induced radical polymerization offers a promising route for the rapid and efficient fabrication of metal-polymer nanocomposites. We present an approach wherein the two radicals produced upon the bond cleavage of Norrish Type I photo-initiators simultaneously undergo radical polymerization and metal reduction. This allows the production of well-defined metal-polymer nanocomposites in a one-step synthesis.

We demonstrate how investigating reaction kinetics can elucidate the synergistic interactions between the photochemical and metal-reducing processes.[1] Additionally, we show how choosing different photo-initiator/monomer/metal combinations can be successfully employed to produce materials with tuneable properties, making them attractive candidates for application in heterogeneous catalysis.[2]



Scheme 1. Alpha-cleavage of a photoinitiator upon irradiation, yielding a polymerizing radical **P•** and a reducing radical **R•**, allowing the one-step synthesis of metal polymer nanocomposites

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NEW SENSITIZERS FOR ACYLPHOSPHINE OXIDES

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The use of long wave sensitizers to activate photoinitiators is well established. For the UV curing industry, this energy transfer effect has already been put to good use, for instance in high speed UV inks. Small additions of isopropylthioxanthone (ITX) to aminoalkylacetophenone photoinitiators such as 2-benzyl-2-(dimethylamino)-4'-morpholino-butyrophenone (Omnirad 369) improve the cure speed by a considerable degree. These systems have been studied in some detail to give a good understanding of the sensitization process[1]. Sensitization of other photoinitiators, such as substituted benzophenones, has also been explored[2]. The currently used mechanism is based on an energy transfer taking place between the triplet states of the sensitizer and the photoinitiator.

For energy transfer to occur only two parameters are critical:

- The triplet energy ET of the sensitizer must be greater than that of the photoinitiator.

- The triplet state of the sensitizer should have a long lifetime (typical of Type II photoinitiators acting as sensitizers).

In this presentation we will describe a new way of sensitizing photoinitiators, focused on acylphosphine oxides.

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Molecules with multiple Bis(acyl)phosphanoxide groups as Photoinitiators, Cross-Linkers, and Inimers

Hansjörg Grützmacher[1], Debora Thöny[1], Riccardo Conti[1], Anna Widera[1], Annalisa Chiaponne[2], Georg Gescheidt[3]…..

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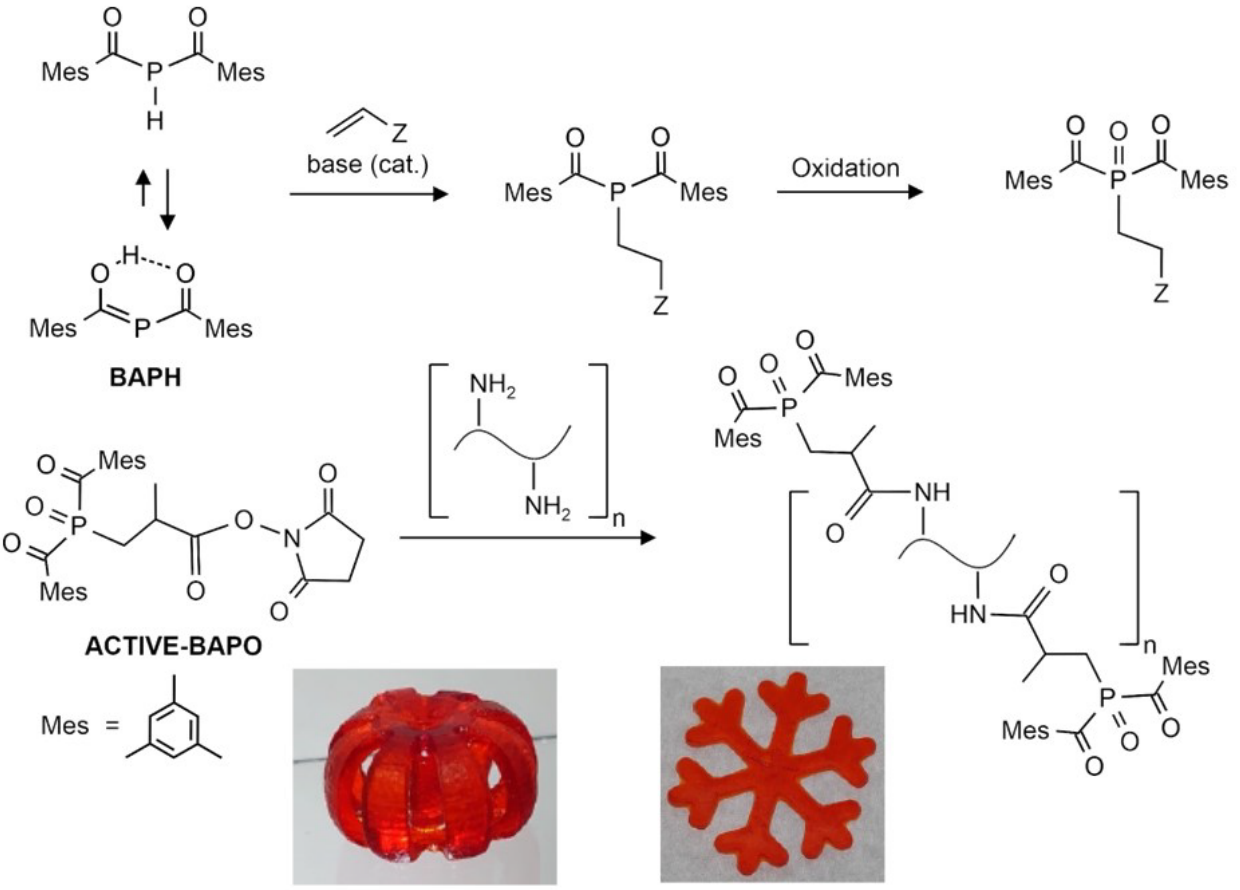
We developed an organocatalyzed Phospha-Michael addition using BAPH[1] and a simple condensation reaction using ACTIVE-BAPO[2] as reagents for the synthesis of tailor-made photoinitiators (PIs), which can be used as multiple PIs, inimers, and cross-linkers. With these materials can be 3D printed, which show superior mechanical properties.



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PREPARATION OF ORGANIC-INORGANIC HYBRIDS BY THIOL-ENE REACTION AND THEIR APPLICATIONS

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Organic-inorganic hybrids are molecularly dispersed nano-composites of organic and inorganic components, which are noted as most attractive materials with the specific characteristics. These materials are expected to have new functions for the versatile advanced applications in many fields. The typical organic-inorganic hybrids can be prepared by a sol-gel reaction of metal alkoxides in organic polymers or with some polymerizations. We have already studied the preparation of organic-silica hybrids using the photo-curable polysilsesquioxanes prepared from the organic substituted trialkoxysilane.[1, 2] The radical and cationic polymerizations are carried out by using the polysilsesquioxane containing acrylic and epoxy groups, correspondingly. And also the polysilsesquioxane with thiol groups would be reacted by Thiol-Ene reaction, which is a radical addition reaction of thiol groups to C=C bond of olefin compounds.

We investigated that Thiol-Ene reaction with thiol-containing polysilsesquioxane and multifunctional allyl compounds produced new type of organic-inorganic hybrid materials, as shown in Fig.1. Thiol-containing polysilsesquioxanes were prepared from the hydrolysis and condensation of mercapto-propyltrimethoxysilane. When triallylisocianate (TAIC) as multifunctional allyl compounds was reacted with the silsesquioxanes under UV irradiation, these obtained hybrid materials had some specific properties such as high transparency, high refractive index, and thick film formation, in addition to low shrinkage after photo-curing. Furthermore, these hybrid materials with multi-thiol compounds showed the self-healing properties of scratched surface.

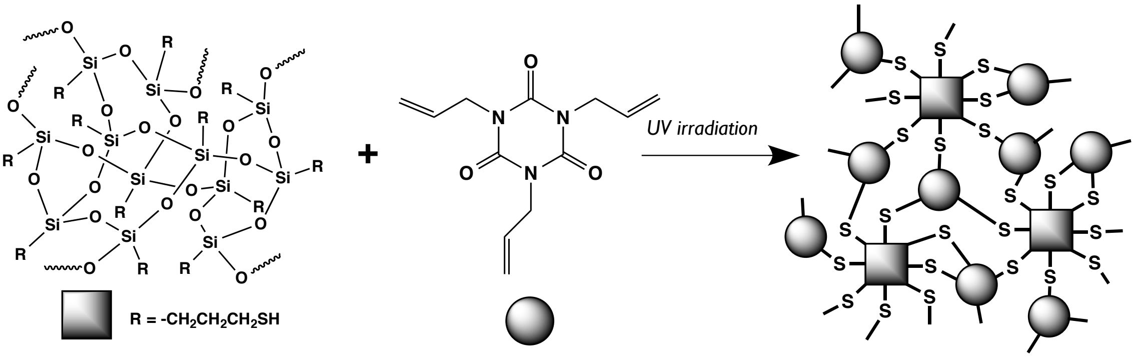

Fig. 1 Preparation of organic-inorganic hybrid with thiol-containing silsesquioxane and TAIC.

As unirradiated part of these hybrids was dissolved easily by using 2.38% aqueous tetramethylammonium hydroxide (TMAH) solution, the behaviour can be used as a negative resist. The unreacted thiol group in polysilsesquioxane can capture Pd catalyst for an electroless plating, so it could be effectively used as a catalyst layer for the electroless Cu plating. Therefore, the fine pattern of electroless Cu plating was formed, which is expected to apply to the fabrication of transparent circuit.

On the other hand, organic-inorganic hybrids can be prepared by dispersing nanomaterials, which is nanoparticles, nanosheets, etc., in polymers. For example, organic-inorganic hybrid materials containing zirconia nanoparticles are most interested in the application for high refractive index coating. As the fine dispersion of zirconia nanoparticles is necessary to prepare the transparent hybrid coating, the surface modification was investigated by using dicarboxylic acid anhydride. Especially, 5-norbornene-2,3-dicarboxylic acid anhydride (NDCAA) exhibited a good surface dispersibility to form the ester bonding with Zr-OH. The internal olefin of norbornene skeleton is a useful component for Thiol-Ene reaction with multi-thiol compounds. The stoichiometric mixture for C=C of NDCAA and TAIC and S-H groups of pentaerythritol tetrakis (3-mercaptopropionate) (PEMP) formed multiple crosslinking structure via Thiol-Ene reaction as shown in Fig. 2. Thus obtained photo-cured materials demonstrated high transparency and flexibility despite the hybrids containing zirconia nanoparticles. The refractive index of hybrid coating could be controlled by the content of zirconia nanoparticles. In the case of 80wt% content of zirconia nanoparticles, it was found that the refractive index quite high (>1.7). On the other, the flexible self-standing films could be prepared from the photo-cured hybrid of 50wt% content of zirconia nanoparticles. Furthermore, the recent results related some applications of hybrid materials with zirconia nanoparticles would be introduced.

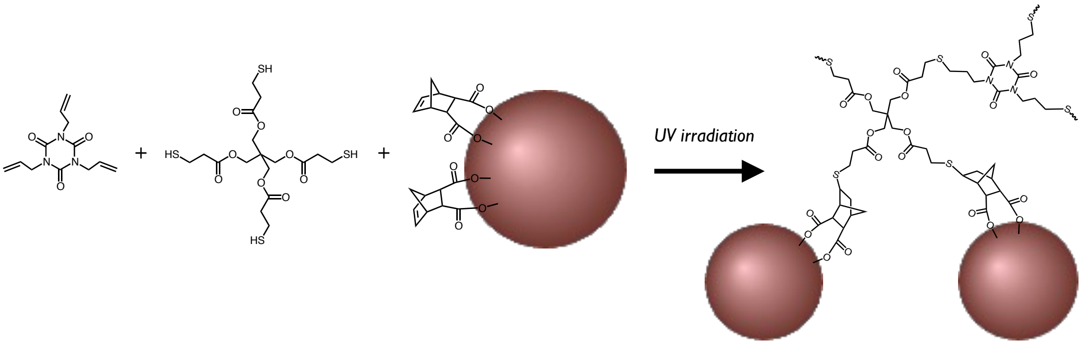

Fig. 2 Preparation of photo-cured hybrids from TAIC, PEMP, and NDCAA modified zirconia nanoparticles.

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New photoinitiating systems and strategies for high performance materials

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Keywords: photoinitiators, photopolymerization, LED curing, dual cure systems

Abstract: Photopolymerization technology has been developing steadily benefiting from the characteristics of spatial and temporal controllability, environmental protection, and efficient processes.[1,2] However, the polymerization in shadow areas remains a huge challenge. In this work, new photoinitiating systems for radical, cationic or hybrid polymerization will be presented for different spectral ranges: near UV, visible, Near Infrared. This work will be extended to dual-cure processes as well as photopolyaddition reactions. Better depths of cure can be obtained. Some applications for coatings, 3D printing and photocomposites will be provided. The mechanical properties of the generated polymers/composites will be also investigated.

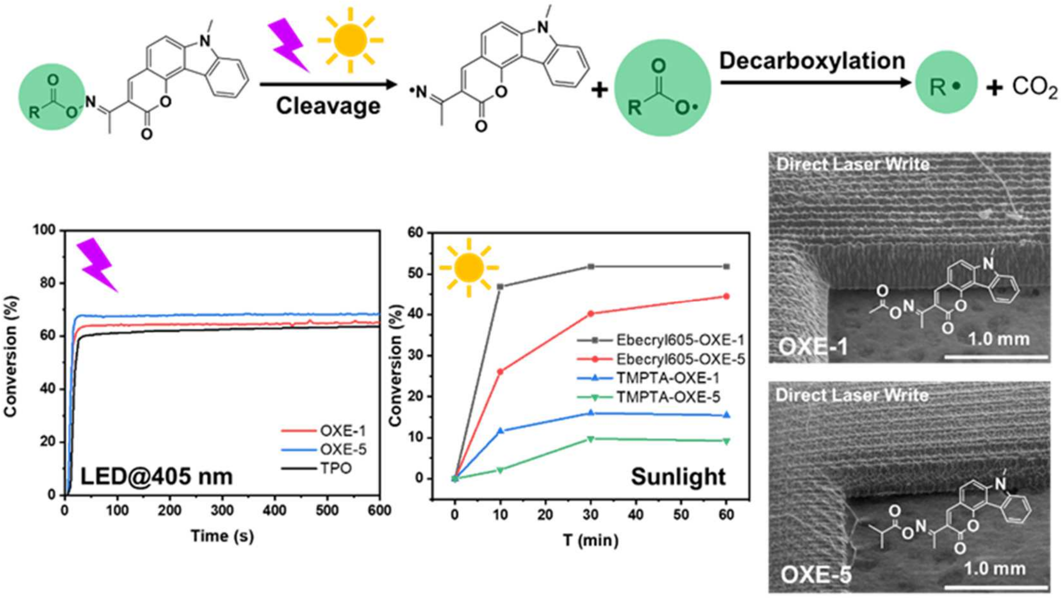

Figure. Example of new high performance photoinitiating systems.

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NEW PHOTOINITIATING SYSTEMS FOR DENTAL APPLICATIONS

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Photo-curing 3D printing technique, despite its arrival on the market a decade ago, is still not very popular in the dental industry. This is because there are expensive and low-performance printing resins on the market, and because of the high cost of printers for the dental industry. Another problem that makes 3D printing unpopular and not widely used in the dental industry is the toxicity of acrylic resins. Material made from acrylic monomers has a lower resistance to damage than, for example, porcelain or all-ceramic crowns used as fixed prosthetic restorations. The acrylic material quickly becomes mechanically damaged, abraded and lacks sufficient marginal tightness, thus easily depositing food particles and bacterial plaque, which can cause inflammation and decay.

Poor marginal tightness between the restoration and the tooth tissue is caused by polymerisation shrinkage of materials designed for temporary crowns and bridges.[1,2] Polymerisation shrinkage is an extremely unfavourable phenomenon in restorative dentistry, as it can cause stress-induced microcracks, poor adhesion of the photo-cured material to the substrate, surface delamination or deformation of shape symmetry.

In this work, new initiator systems for potential use in photo-curable 3D printing for dental applications were presented. Spectroscopic and kinetic studies of new photoinitiating systems were carried out and the most efficient systems for 3D printing were selected.

Acknowledgements

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Synthesis of innovative type I photoinitiators for free radical photopolymerization induced by visible light and studies of their application to 3D printing

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Photopolymerization processes are one of the most efficient methods for obtaining polymeric materials and, in addition, it is still a rapidly developing field. The most commonly used method of polymerization using light is radical photopolymerization[1]. Initially, the photopolymerization process was carried out using UV light. Today this process is gaining importance in other industries, e.g. in photolithography, medicine, and microelectronics, and the fastest development of this technology is in 3D printing. Unfortunately, these industries severely limit the possibilities of using photoinitiators operating in the UV range. This is due to the harmfulness of this radiation to humans, or in the case of 3D printing, the inability to achieve adequate depth of cure[2]. In opposition to UV process, a better light penetration can be achieved with visible light. On an example of polystyrene latex, observed was that at irradiation with light at 320 nm, penetration of light is limited to 600 µm. In comparison, by using light sources with an emission maximum at 450 nm, 4 mm layers was obtained[3].

Based on the above, we have developed a new approach to obtaining radical photoinitiators. The novel photoinitiators were obtained by "modification of benzil ketals" due to the extension of their conjugation structure. Modification of the mentioned initiator allows to shift spectrum toward longer wavelengths making the new systems active under the LED with emissions maximum at 405 nm, 415 nm, or maybe even at 430 nm and higher which is rarely seen today. The efficiency of the developed systems has been tested through extensive spectroscopic studies. The photodecay capability of the novel photoinitiators was investigated in photolysis tests using light sources with emissions corresponding to 405 nm or higher. The ability to initiate the radical photopolymerization process was then investigated using real-time FT-IR and compared to a commercially available analog, 2,2-dimethoxy-2-phenylacetophenone (Irgacure 651/DMPA). Acrylate systems were tested using trimethylolpropane triacrylate (TMPTA) monomer as an example. Thiol-ene systems were tested based on 1,3,5-triallyl-1,3,5-triazinane-2,4,6-trione (TATATO) with trimethylolpropane tris(3-mercaptopropionate) (MERCAPTO) formulations. Additionally, urethane-dimethacrylate (UDMA) with the addition of triethylene glycol dimethacrylate (TEGDMA) formulation was tested. The ability to initiate the photopolymerization process was tested using light sources with emission maxima of 365, 405, 415, 455, and 470 nm on both thin (25 µm) and thick films (1,5 mm). Compared to DMPA, which showed no activity at 455 nm and very low activity already at 415 nm, some of our photoinitiators worked efficiently even at 470 nm. The above studies were confirmed during application tests using VAT 3D printing.

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WAVELENGTH-DEPENDENT PHOTOCHEMISTRY OF ACYLGERMANE PHOTOINITIATORS

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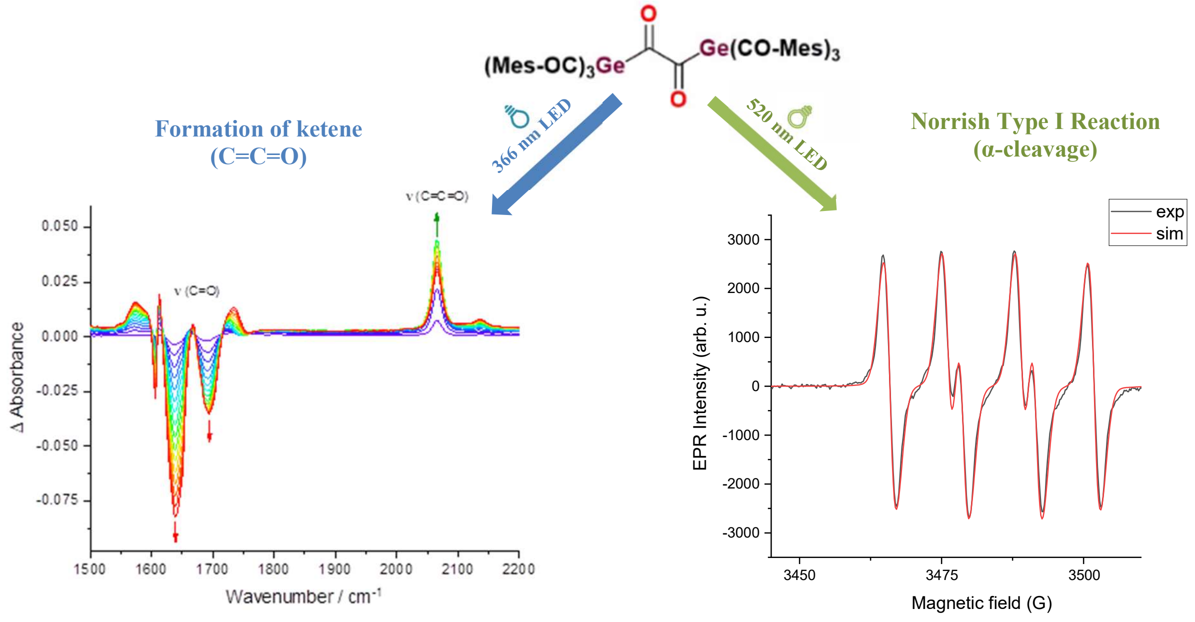
The majority of state-of-the art visible light photoinitiators like acylphosphines, acylstannanes and acylgermanes decompose into radical species via Norrish type I reaction (α-cleavage). [1] When short lived radicals are formed, ^{1}H-CIDNP (chemically induced dynamic nuclear polarization) spectra recorded in the presence of a monomer show polarized NMR signals (either enhanced emission or adsorption) and formation of aldehydes. [2] In the case of our studied 1,2-bis(tris(2,4,6-trimethylbenzoyl)germyl)ethane-1,2-dione and hexakis(trimethylsilyl)digermane no polarized signals and no formation of aldehydes was detected. That´s why we decided to study these new germanium photoinitiators with various spectroscopic techniques like IR, UV-vis, EPR spin trapping and NMR to understand their photoreactivity. Our results so far show that the behaviour of 1,2-bis(tris(2,4,6-trimethylbenzoyl)germyl)ethane-1,2-dione differs in the presence of blue and green visible light. By the use of 520 nm LED source (green light) we could see the standard α-cleavage-type of reaction forming DMPO-benzoyl radical adducts in the EPR. On the other hand, time-resolved IR spectra have shown that shorter wavelengths like 355 nm LED (blue light) results in a specific rearrangement in the structure – formation of a ketene.



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NEW NAPHTHALENE IMIDE BASED INITIATORS FOR PHOTO-ATRP

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Naphthaleneimide (NI) derivatives represent a class of organic compounds with diverse applications, ranging from materials science to medicinal chemistry.[1] They can be incorporated into polymers, supramolecular assemblies, and coordination complexes to impart desired properties such as enhanced stability, fluorescence, or conductivity.[2] Therefore, two naphthalenimide derivatives were proposed in the form of alkyl bromide initiators, serving as potential initiators for photochemically induced atom transfer radical polymerization (photo-ATRP).[3] Third acetylated naphthalene imide was chosen as a probe to investigate the potential effect of its presence on polymerization and to elucidate the mechanisms involved. These NI compounds should not affect the polymerization mechanism itself since they absorb a different wavelength of light than that required for polymerization. They should serve as fluorescent markers at the beginning of the polymer chain, for studying the mechanism of photo-ATRP in terms of initiation efficiency. Therefore, they provide a more sensitive system to study the initiation efficiency and viability of photo-ATRP through a combination of GPC and fluorescence detectors. In the case of light absorption used in photo-ATRP, a photoactive initiator can increase the initiation efficiency by absorbing light and converting it to energy in the initiation phase of polymerization. Furthermore, they confirm the feasibility of preparing fluorescent materials one step photopolymerization. Conversely, when using an initiator lacking a fluorescent label, additional modification becomes necessary. The named initiators were prepared, characterized, and applied for the first time in photoATRP during the polymerization of methyl methacrylate, and methyl/*n*-butyl acrylate in various solvents in the presence of air, with subsequent monitoring of the fluorescence label in the polymers. The living end of the polymer was also confirmed by the preparation of short oligomers as macroinitiators, which were subsequently subjected to elongation reactions.

Acknowledgment

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NIR-Sensitive Systems Comprising Cyanines Operating as Molecular Oven to Facilitate Photopolymerization in the Shadows and Physical Drying

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NIR-light mediated processes have received increasing interests due to its benefits of deeper penetration of excitation light into the samples compared to UV sensitive systems and the broader accessibility of working wavelength. Cyanines comprising variable structural patterns play vital role as light absorbers with broad absorption wavelength in near-infrared range between 700-1100 nm in photochemical reactions based on activated photoinduced electron transfer (**PET**). The technology of high-power NIR-LED prototypes was recently introduced to the photopolymerization systems promoting to overcome the internal activation barrier in the cyanine-comprising systems exhibiting a positive charge. Therefore, the combination of high-power NIR-LEDs and cyanines facilitates the process by dual initiation mechanism where initiating species (reactive short-living radicals and conjugate acid) formed, and heat generated from the cyanines contribute to polymer fabrication. The initiating systems comprising cyanines and iodonium salts carrying $N(SO_2CF_3)_2^-$ as counter ion showed significant efficiency to initiate radical polymerization using UDMA and 4-hydroxybutyl vinyl ether for cationic polymerization, respectively, as determined by real-time FTIR. Surprisingly, the heat generated from cyanines upon exposure also promotes the diffusion of the radicals formed by **PET** reaction between iodonium salt in the matrix using (meth)acrylates as monomers facilitating radical photopolymerization also occurring in the shadow resulting in formation of homogeneous polymer networks. The mechanical properties of the materials obtained in the shadow showed similar performance compared that from exposed areas, while the materials processed in an oven exhibited different behaviour. This again approves that the dual combination of photonic events and heat contributed to the materials properties in the shadow of the exposed object. Furthermore, such systems also facilitate the physical drying of coating dispersions for removal of water as a replacement of conventional oven techniques followed by radiation with either UV or NIR light for crosslinking. This ON/OFF process can be seen as a big benefit for energy saving.

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INVESTIGATION OF NOVEL LONG WAVELENGTH PHOTOINITIATORS FOR RADICAL POLYMERIZATION

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Photoinitiators (PI) for free radical polymerization have been modified using heteroatoms in the α-position to the benzoyl chromophore since the 1980s.[1] At that time, acylphosphine oxides were introduced, originally for an application in the coating industry.

Further investigations led to the discovery of Ge-based PIs, with diacylgermanes showing particularly good properties.[2] These molecules show the desired bathochromic shift in the absorption spectra, what enables the use of light with longer wavelength. This red-shifted light is important for enhancing the curing depth of formulations.

The current state-of-the-art PI is also located in the diacylgermane family with the trade name Ivocerin®. Additional advantages of Ivocerin® are thermal stability and low toxicity. Nevertheless, Ge-based PIs are higher in price compared to e.g. phosphorus based PIs, and therefore not for every application suitable. One way to overcome this disadvantage are Sn-based PIs, as this substance class is known to reach excellent bathochromic shifts in their absorbance as well as high reactivity.[3] The only drawback is the poor storage stability of the so far known Sn-based PIs.

In this work, novel Ge as well as Sn-based PI were successfully synthesized and photochemically investigated including UV/Vis measurements, photo-DSC measurements and steady state photolysis experiments in order to compare their photochemical properties as well as stability with literature known Sn-based PIs.

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UNVEILING THE POTENTIAL OF PHOTOBASE IN PHOTOSYNTHESIS OF GOLD NANOPARTICLES IN ORGANIC SOLVENT

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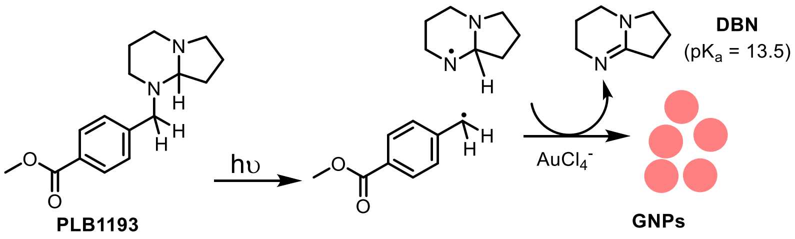
Gold nanoparticles have attracted the greatest interest in nanoscience and nanotechnology due to their intriguing electronic, chemical, and optical properties (notably plasmonic effects)[1]. In this study, we introduce a novel and scalable photochemical method for synthesizing small-sized gold nanoparticles in alcoholic solvents, employing a photolatent base or photobase for the first time. The process relies on the use of an oil-soluble photobase derived from an amidines base (namely PLB1193, as shown in scheme below). Under UV-irradiation, this photobase undergoes Norrish type I cleavage, generating primary radicals and subsequently releasing a strong base [2,3]. These radical species play a key role in reducing gold ions to their atomic form, facilitating nanoparticle growth. The influence of solvent types, stabilizer, irradiation parameters were systematically studied under batch conditions, which has been successfully translated into a commercially available photochemical reactor. Furthermore, we also demonstrated that PLB1193 is a straightforward and efficient reducing agent for preparing gold nanoparticle in acrylate resins, opening the door to nanocomposite applications. The method outlined in this research paves the way for numerous opportunities to explore the potential applications of photobases and photoacids for the preparation of gold and potentially other noble metal nanocomposites.



*Scheme**Error! No text of specified style in document.**-1 Photochemical cleavage of the amidine derivative PLB-1193 to release of DBN and simultaneous preparation of GNPs*

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DESIGN OF BIOBASED UV CURABLE FORMULATIONS FOR 3D PRINTING

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Over the past few decades, the development of polymeric materials derived from bio-renewable sources has grown significantly, driven by the environmental challenges that the planet is facing. Moreover, the depletion of oil, which is the primary carbon resource for polymer synthesis, has stimulated in-depth research into alternative sources that have a reduced environmental impact. Indeed, most resins processable through VAT polymerization techniques are obtained from fossil sources. An interesting green alternative is represented by vegetable oils (VO), which can be easily functionalized thanks to the presence of numerous insaturations and their high availability at low cost. Among these, soybean oil is one of the most used thanks to the possibility of being functionalized through epoxidation and subsequent acrylation to obtain acrylated epoxidized soybean oil (AESO). Besides VO there are other possibilities, like glycerol-based polymers, which can be acrylated to make them sensitive to UV light. In this work, different types of formulations based on AESO [1] and polyglycerol-based acrylic monomers [2] (by Sakamoto Yakuhin Kogyo Co., Ltd.) were characterized and tested as feed materials for digital light processing (DLP). Reactivity, rheological properties, and visco-elastic properties of these two kinds of formulations have been investigated. Additionally, complex shaped objects were printed to determine the accuracy of the printing process with these formulations.

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BIO-BASED RESINS: REVIEW AND CHARACTERIZATION OF A NEWLY SYNTHESIZED FORMULATION

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The incorporation of biomass feedstocks is essential for the advancement of sustainable materials as substitutes for fossil-based resources. In this context, furan derivatives have been explored as promising bio-based building blocks components. In our research, two specific furan derivatives, 2,5-Furandimethanol (FDM) and cis-cyclobutane-1,2-dicarboxylic acid (CBDA), both of which were derived from Furylacrylic acid, were selected as starting point. An allylation was performed to modify the hydroxyl (-OH) groups of FDM and CBDA into allyl groups (C=C). The resulting bis-allyl derivatives were blended with commercially available tris- and tetra-functional thiol compounds and cured using UV light through a thiol-ene reaction. The UV-curing process was comprehensively examined using real-time FT-IR, photo-DSC, and photo-rheology methods to investigate the curing kinetics. Subsequently, the resulting bio-based thermosets' thermal-mechanical behavior using DMTA and tensile testing were analysed. The outcomes revealed similar properties to previously investigated bio-based thiol-ene thermosets, suggesting the potential application of the studied material in coating applications.

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EPOXY BIO-BASED MONOMERS FOR UV-CURING

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Biomass feedstocks are playing a crucial role toward the development of new sustainable materials with the aim to replace the fossil-based ones limiting the emissions and waste. Among the other, cellulose, hemicellulose and lignin are gaining interest as a source of new bio-based building blocks [1]. Indeed, lignin and cellulose represent interesting base platform to derive several monomers which can be further functionalized becoming interesting for UV-curable applications. The necessity to limit energy consumption and time lead to the innovation of production processes and the UV-technologies have gained interest to provide a valid alternative to traditional thermal curing in the production of thermosets. In this framework epoxy chemistry can fruitfully combine the use of green monomers and UV to develop new bio-derived formulations. Several green monomers have been exploited, from furan-based monomers [2] to isosorbide-based one [3]. Distinct applications have been covered spreading from coating technology to 3D printing [4]. The starting monomers were functionalized and fully characterized by NMR analysis. Then, UV-curable resins were formulated and the reactivity toward UV-light was tested by different techniques, from photo-DSC to real-time FTIR. Thermo-mechanical and mechanical properties of the green thermosets were assessed through DMTA, DSC and tensile analysis. Regarding the 3D printing applications, a comprehensive investigation of printability and final properties was carried out, while considering the coating applications, surface properties, such as adhesion, contact angle, hardness were studied.

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PHOTOINITIATED RADICAL POLYMERIZATION OF BIO-BASED METHACRYLATES

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Bio-based monomers made from plant materials have received increased interest recently because plants are seasonal renewable although fossil resources, which are still the main source for monomer manufacturing, will be limited available in the future. Methacrylates are synthesized directly from hydroxy-substituted bio-based starting material on the one hand and from bio-based epoxy compounds that are made e. g. by epoxidation of unsaturated bio-based compounds on the other hand.[1-4] Photoinitiated polymerization of the bio-based methacrylates combines the bio-based monomers with an environmentally friendly and energy efficient polymerization method.

Ethylphenyl-(2,4,6-trimethylbenzoyl)-phosphinate (Irgacure® TPO-L) was selected as photoinitiator for the photoinitiated radical polymerization of the bio-based methacrylates. In case that the methacrylate is crystalline at room temperature and melts at higher temperature, photoinitiated polymerization was investigated at higher temperature. Photo-DSC investigation shows significant differences in the photopolymerization kinetics between the bio-based methacrylates, which are substituted with a hydroxy group or a carboxylic group in addition to the methacrylate group. The latter is bound either in the middle of an alkyl chain or at one end of a longer alkyl chain similarly to commercial dodecyl methacrylate. Furthermore, final conversion is higher for the bio-based methacrylates compared to commercial dodecyl methacrylate. This is a big benefit of the bio-based methacrylates in comparison with commercial dodecyl methacrylate. Depending on the additional substituents, the photopolymers obtained from the bio-based methacrylates are either crystalline or glass forming materials. This makes them interesting for application e. g. in coatings.

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EXPLOITATION OF TANNIC ACID AS ADDITIVE FOR THE ADHESION ENHANCEMENT OF UV-CURABLE BIO-BASED COATING

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Nowadays, great attention has been focused on the development of environmentally friendly and sustainable coatings. Within this framework, the exploitation of bio-renewable and natural sources and green polymerization techniques is growing [1]. UV-curable coatings from several vegetable oils, like epoxidized soybean oil (ESO), have been proven potential alternatives to the traditional coating systems [2]. However, the improvement of UV-cured bio-based coatings adhesion has become one of the key issues and natural polyphenols have been revealed to be prominent sustainable adhesion promoters [3].

The current work investigated the natural tannic acid (TA) as an additive to enhance the adhesion performance of the UV-curable ESO-based coating on a low-carbon steel. To homogeneously disperse the tannic additive into the coating formulation, TA solutions with two different concentrations were prepared and added with different weight ratios. The assessment of cationic photopolymerization was performed through real-time FTIR and photo-DSC analyses. The TA addition significantly increased the epoxy group conversion thanks to a chain-transfer process, named activated monomer mechanism [4], which involves the multiple phenols of TA. After 90 s of UV exposure, the conversion of ESO/TA coatings reached around 90%, while the pristine ESO formulation, without the tannic additive, showed a conversion of about 72%. Nevertheless, the DMTA showed that the coating crosslinking density reduced as the TA amount increased due to the activated monomer mechanism. Lastly, the tannic additive remarkably enhanced the UV-cured ESO coating adhesion property on low-carbon steel substrates as the TA polyphenols can coordinate iron. Moreover, the steel surface pretreatments influenced the adhesion performance. Indeed, an outstanding adhesion with the tannic additive was found both for the pickled steel samples and on the steels pretreated with the more safe and eco-friendly plasma technique.

In conclusion, a noteworthy adhesion improvement on low-carbon steel was achieved by the addition of natural TA into a UV-curable bio-based coating. The tannic additive participated in the photocrosslinking reaction with the enhancement effect on the conversion and coordinated iron on the steel surface, acting thus as a “bridge” between the sustainable coating and the metallic substrate.

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EXPOLITING 3D PRINTING FOR BIOACTIVE GLASS REINFORCED BIOBASED SCAFFOLDS

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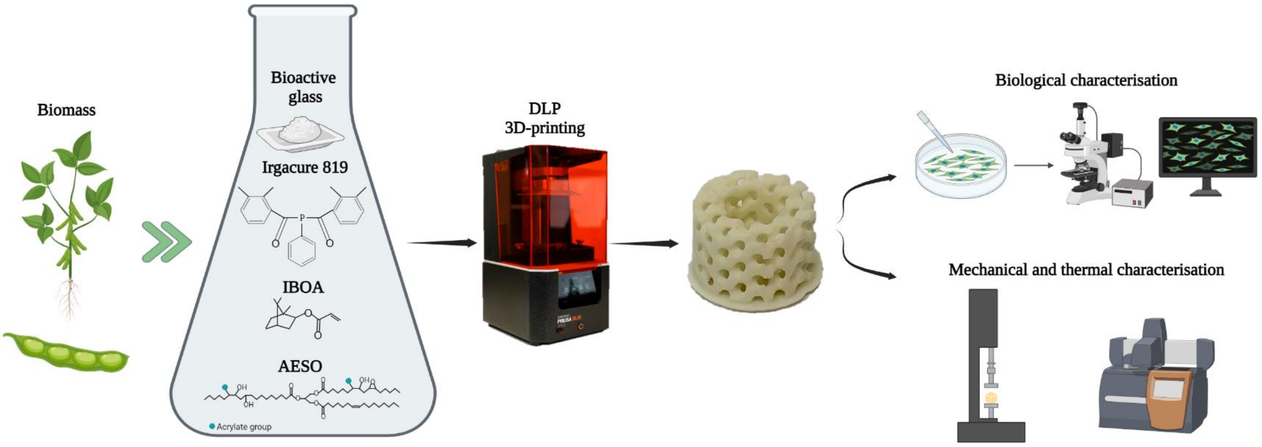
In our study, we designed a bio-based formulation based on soybean oil, and exploit to obtain scaffold filled with bioactive glass particles. Our formulation included acrylated epoxidized soybean oil (AESO), isobornyl acrylate (IBOA), a photo-initiator (Irgacure 819), and bioactive glass particles synthesized on purpose. By using UV light, the resin was photopolymerized, and the crosslinking process was monitored. Even in the presence of bioactive glasses the curing process achieved a high conversion.

We also explored the printability of the photocurable formulation. The objects we printed were compared to those manufactured in silicon molds, revealing different qualities. This comparison highlighted the positive effect of 3D printing, which, in addition to being a versatile and accessible technology, allowed us to produce specimens with improved characteristics. The schematized process is reported in Figure 1.

Figure 1: Scheme of the process from photocuring to 3D-printing of the bio-based photocurable formulation



Bioactive glass dispersion was verified through SEM, confirming even distribution within the matrix. To understand how our scaffolds interacted with living cells, we conducted a comprehensive biological analysis. We utilized human bone marrow mesenchymal stem cells (bMSCs) to evaluate the compatibility and suitability of our scaffolds for cellular growth.

In the end, our study demonstrates a new way to manufacture bioactive glass scaffolds using 3D printing, offering promising avenues for applications in tissue engineering.

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Bio-based and Recycled Materials for UV Applications: A Sustainable Approach to Photopolymer Technology

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This paper explores the integration of bio-based and recycled materials in ultraviolet (UV) applications, with a specific focus on their role in advancing photopolymer technology. Photopolymers, widely used in UV-curing processes for coatings, adhesives, and inks, traditionally rely on petroleum-based feedstocks, contributing to environmental concerns. The study investigates the viability of bio-based materials, such as plant-based polymers and agricultural waste, as sustainable alternatives. Key considerations include biocompatibility, mechanical properties, and UV sensitivity in formulating UV-curable materials.

Additionally, the paper delves into the use of recycled materials to promote circular economy principles in UV applications. It assesses the potential of recycled polymers in terms of UV responsiveness and their impact on the overall performance of cured materials. Environmental implications, including reduced carbon footprint, energy consumption, and waste generation, are considered in adopting these sustainable practices.

By addressing challenges and advancements in incorporating bio-based and recycled materials, this research contributes to the ongoing efforts in reducing the environmental impact of photopolymer technology. Furthermore, the paper discusses the economic feasibility and scalability of these sustainable practices, encouraging wider adoption within the industry. Ultimately, this exploration aims to foster a more sustainable future for UV-curable materials, aligning with global initiatives to mitigate resource depletion and environmental pollution.

Sustainable Photoinitiating Systems Derived from Biomass. Type I + II Photoinitiators for Free Radical Polymerization, and Light-Mediated ATRP

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Different biomass served as raw material for synthesizing Carbon Nanodots (**CD**s). Their different origin resulted in different efficiencies for free radical polymerization and a photo-ATRP setup using as co-catalyst either $CuBr_2$ or $FeBr_3$ at a scale <100 ppm. Alternatively, a metal-free approach also successfully worked with **CD**s available from hemicellulose linked in an organic network and confined **CD**s obtained from cellulose in a silica-confined network. The latter exhibited a room temperature phosphorescence (**RTP**) greater than 100 ms, indicating triplet state formation as a new concept. The triplet state connects the system to a metal-free photo-ATRP reaction protocol, while systems with no efficient triplet formation failed. Lignin itself was also found to work in a photo-ATRP setup using $CuBr_2$ as a metal co-catalyst. Photocatalysts derived from *Kerria lacca* resulted in the lowest value; that is ≈1.1, using Cu(TPMA)Br2 in a range of <100 ppm and Ethyl-α-bromo phenylacetate as initiator. Confined CDs derived from cellulose worked in the photo-ATRP at a level of only 9 ppm, resulting in a small dispersity of the polymers obtained. The polymers obtained exhibited a different dispersity of molecular weight depending on the biomass origin of the **CD**.

Alternatively, hydrothermal treatment of furfural available from hemicellulose provided **CD**s with aldehyde groups on the surface. These structural patterns also enabled covalent binding of photoactive groups resulting in homolytic cleavage of the attached group upon UV exposure. This connects to Type I photoinitiators whose photoinitiating properties will be shown at this conference for the first time. The low cytotoxicity of the **CD**s was also remarkable.

Furthermore, results obtained demonstrated the use of a sustainable photocatalyst with multiple purposes comprising demethylated lignin (**Fe_3O_4@D-wood**). This was made by the treatment of wood and iron oxide. The same material became the subject of photocatalytic explorations for water treatment and material synthesis by radical photopolymerization opening the door to materials facilitating multiple uses for different purposes. Exposure of **Fe_3O_4@D-wood** with artificial sunlight showed an improved activity considering the photochemical oxidation of organic pollutants in the presence of H2O2. The efficient generation of reactive radicals brought this system also to photopolymerization. Here, radicals based on reactive oxygen species (**ROS**) generated in the catalytic cycle can be seen as the dominating species to initiate radical polymerization. A mixture of UDMA and TPGDA showed good reactivity with cumene hydroperoxide (**CHP**). Photocatalyst used for water treatment facilitates reuse for photopolymerization.

Oxime esters : highly efficient photoinitiators for overcoming oxygen inhibition in 3D-inkjet priting applications

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Abstract

A series of four commercially available oxime esters were studied as Type I photoinitiators. Initially, their UV-visible absorption properties were examined, revealing significant absorption in the near-UV range, with some also exhibiting absorption in the visible range. Photopolymerization kinetic studies were conducted using the Real-Time Fourier Transform Infrared (RT-FTIR) technique, employing various light sources (UV lamp, LEDs at 365 and 395 nm) for samples of 12 µm and 2 mm thicknesses under ambient air conditions. These experiments demonstrated that all four photoinitiators facilitated efficient polymerization, particularly under conditions of high oxygen inhibition (seen prominently in 12 µm thick samples under air). These oxime esters undergo a photocleavage reaction and decarboxylation, resulting in the release of carbon dioxide (Figure 1) [1]. The release of CO_2 was monitored through RT-FTIR experiments. Results indicate that the oxime esters outperformed certain common phosphine oxides, such as Phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (BAPO). Molecular modeling calculations were employed to determine the enthalpy of cleavage reactions from both singlet and triplet states, revealing favorable cleavage from both energy states. Electron spin resonance spin-trapping experiments were also carried out to investigate the generation of free radicals, contributing to an understanding of the structure-reactivity relationship. Moreover, the oxime esters were tested in 3D-inkjet printing applications, displaying highly promising results with tack-free surfaces. Additionally, these oxime esters exhibit the potential for thermal initiation at moderate temperatures (150°C), offering a dual-curing behavior (Figure 1).

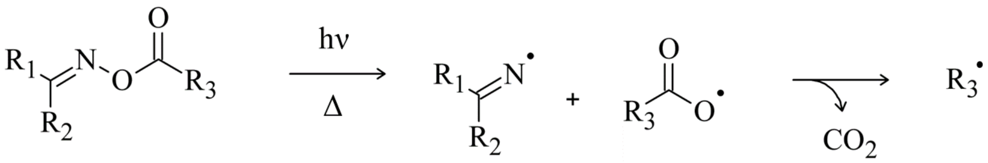

Figure 1. Mecanism of cleavage and decarboxylation of oxime esters [1]

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A NOVEL DISULFIDE-CONTAINING MONOMER FOR PHOTOINITIATOR-FREE SELF-HEALABLE PHOTOCURED COATINGS

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In recent years, UV-curable coatings have slowly replaced solvent-based ones, mainly due to their sustainable features such as low energy consumption and fast curing process. Crosslinked photocured networks containing linear disulfides have attracted a lot of attention due to the peculiar properties and responsiveness of S-S bonds[1], which make them suitable for several applications, chief among them self-healable materials[2,3]. Indeed disulfide bonds are recognized for their sensitivity to several stimuli, and cleavage of disulfide with the formation of thiyl radicals could be easily achieved.

Based on these distinctive features, herein a novel photocurable diacrylated polyurethane monomer containing disulfide bonds (DSPDA)[4] was synthesized through a one-step process without the need for further purification. The photopolymerization kinetics of the monomer was studied through real-time FTIR, highlighting a fast and complete conversion. High acrylate conversions were reached even in the absence of a photoinitiator, thus demonstrating the self-initiating capabilities of the synthesized monomer thanks to disulfide cleavage and thiyl radicals generation upon UV light exposure. Clear coatings were produced using DSPDA monomer and disulfide dynamicity was exploited to obtain self-healing of surface scratches after heat application.

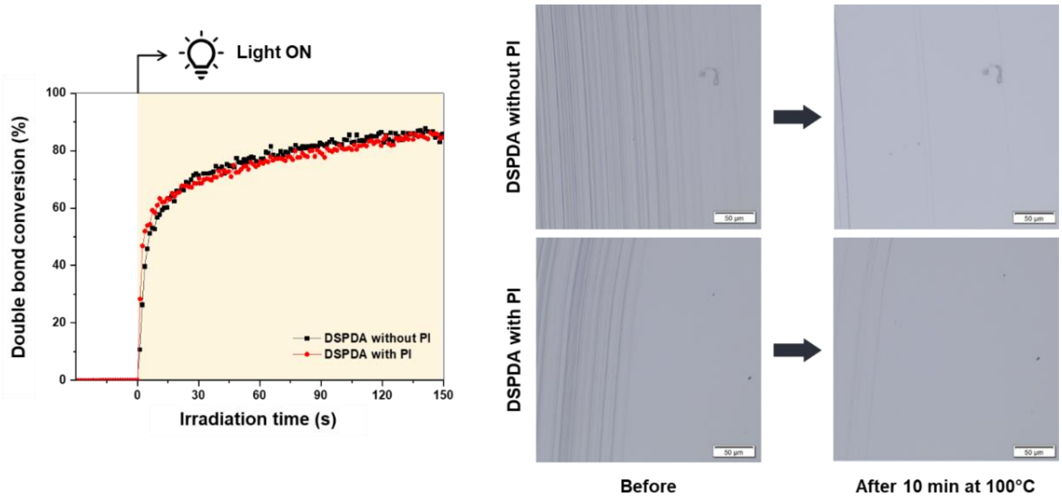

Figure 1: Photocuring kinetics of DSPDA (left) and self-healing of surface scratches in DSPDA coatings (right)

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PHOTORESPONSIVE COVALENTLY LINKED DEXTRAN NETWORKS – TOWARDS FUNCTIONAL HYDROGELS

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Functional materials that can take up and release guest molecules upon stimulation with light can find applications in the area of targeted drug release. [1] Such systems are often based on azobenzene, a molecular photoswitch that can be photoisomerized between its *cis* and *trans* isomers. [2] The bacterial polysaccharide dextran and its modifications have been used in a wide variety of drug delivery systems. [3]

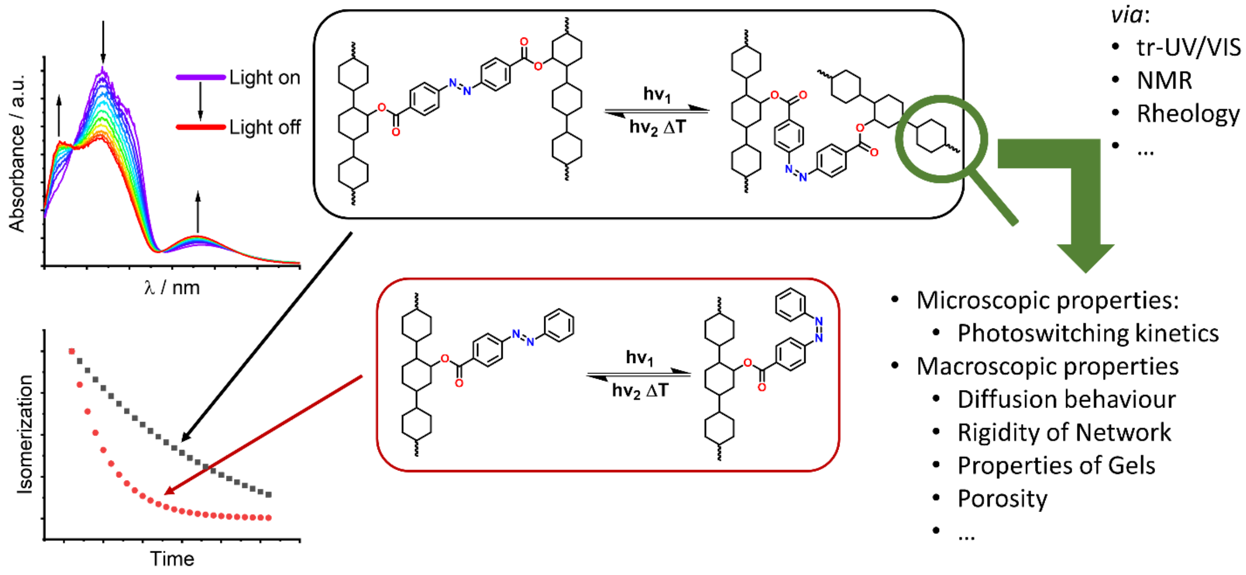

Figure 1: Azobenzene-crosslinked dextran molecules show photoswitching activity, paving the way towards photo-triggered catch-and-release devices.

Here a previously unreported doubly-covalent ester link by azobenzene moieties opens the way for a photo-triggered porous device for the release and capture of small molecules. We have been exploring the potential of such materials by varying the degree and fashion of crosslinking. The preparation of gels with photoswitchable mechanical properties *via* this procedure has been demonstrated.

Control experiments indicate remarkably different material properties when the azobenzene linker is attached by one or two covalent bonds. We have been following the kinetics of *trans*↔*cis* isomerizations of the azo-moiety and the micro- and macroscopic properties of the crosslinked dextran network using a wide variety of analytical techniques, including time-resolved UV/VIS spectroscopy, NMR spectroscopy and, in the case of gels, Rheological measurements.

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Photocrosslinking Enabled by 1,2-Dithiolanes for Dynamic and Responsive Materials

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The design of materials that possess characteristics of both thermoplastics and thermosets has played a pivotal role in transforming conventional polymeric materials. By employing covalent adaptable networks (CANs), the mechanical benefits of crosslinked materials such as toughness and dimensional stability can be effectively blended with the self-healing and reprocessing capabilities associated with non-crosslinked thermoplastics. Seeking to expand on the chemistries used for the deployment of dynamic covalent bonds in networks, we utilize 1,2-dithiolanes, a ring strained cyclic disulfide, for the photopolymerization of CANs. These molecules have been long known to undergo ring opening polymerizations, but their applications in materials have been limited until recently.[1] This ring opening reaction of the dithiolanes directly results in the dynamic linear disulfide moiety at the crosslink.[2] Because of the ring strain, these moieties absorb light and are inherently photoreactive, and thus are capable of polymerization with or without exogenous initiator.[3] The resulting disulfide bonds are capable of multiple actions and respond to varied stimuli. Using dithiolane-functionalized monomers, we form disulfide crosslinks under mild conditions through the photoinduced ring-opening polymerization. These versatile materials present another addition to the CANs toolbox for smart, stimuli responsive materials.

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FROM RING-OPENING POLYMERIZATION OF *N*-CARBOXYANHYDRIDES TO USING LIGHT FOR PREPARATION OF SYNTHETIC POLYPEPTIDES

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Ring-opening polymerization (ROP) of α-amino acid *N*-carboxyanhydrides (NCAs) provides a highly modular platform and expedient route for the preparation of synthetic polypeptides. Light is an attractive trigger for polymerization as it can be controlled both temporally and spatially, and photoinduced polymerizations have become an important technology for advanced manufacturing of polymers.

In this work, we show two different approaches for the preparation of synthetic polypeptides using light. In the first approach, we prepare a polypeptide macromonomer by ROP of NCA and functionalize its chain ends with photoresponsive groups (Figure 1A). In this way, we cross-linked allyl-functionalized poly(γ-benzyl-L-glutamate) (PBLG) 3-arm star macromonomer with trimethylolpropane tris(3-mercaptopropionate) in a high internal phase emulsion by thiol–ene photopolymerization under UV irradiation [1]. By combining the PBLG macromonomer with an allyl-functionalized 3-arm star poly(ε-caprolactone) macromonomer, we obtained polypeptide–polyester materials with tunable termomechanical properties and a polypeptide–polyester bilayer material. The second approach uses light to trigger the ROP of the NCA monomers (Figure 1B). For this purpose, we used photocaged amines that release basic catalysts upon illumination. We investigated the polymerization of γ-benzyl-L-glutamate NCA triggered by the photoreleased catalysts and shed the light on photochemistry of the NCAs.

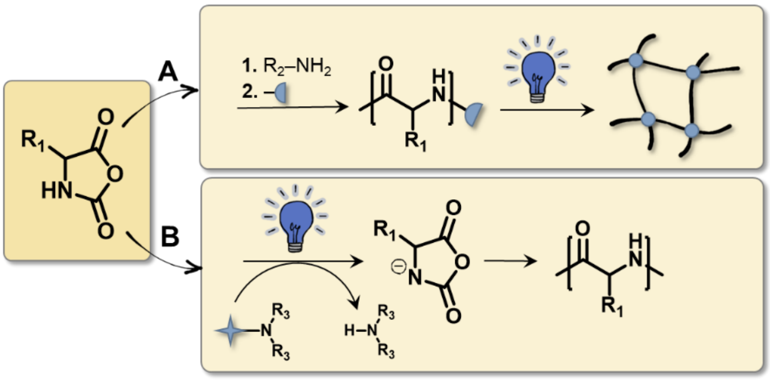

Figure 1. Using light for preparation of synthetic polypeptides. (A) Photocross-linking of chain end functionalized synthetic polypeptide prepared by ROP. (B) Photoinitiated ROP of NCA using a photocaged amine.

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AN ENZYMATICALLY CLEAVABLE PHOTORESIN FOR VOLUMETRIC BIOPRINTING OF LIVING HYDROGEL CONSTRUCTS

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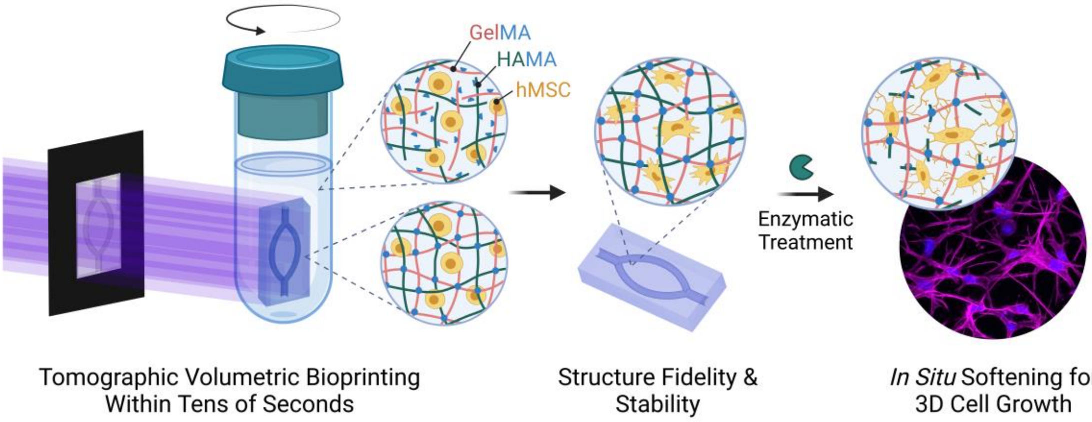
† denotes equal contribution

Volumetric bioprinting (VBP) is an enabling technique to rapidly fabricate complex cell-laden hydrogel constructs through tomographic photopolymerization in a single step. However, it remains a challenge to design a photoresin that combines good printability as well as the ability to support cell growth in 3D. Previous reports in VBP have predominantly used gelatin methacryloyl (GelMA) bioresins.[1-2] Yet, improving printing fidelity often comes at the cost of increasing polymer content and gel stiffness, which inevitably impedes cell spreading. Furthermore, VBP at high cell densities is difficult due to light scattering. Inspired by a recent report,[3] we employ a molecularly cleavable photoresin consisting of GelMA and hyaluronan methacrylates (HAMA), which allows for *in situ* softening of constructs after VBP by enzymatic treatment. Additionally, the refractive index of this photoresin can be fine-tuned using iodixanol to enable VBP at higher cell densities.

Multiple resin compositions were formulated and screened by *in situ* photo-rheology and mechanical testing. Among those, 5% GelMA + 0.5% HAMA + 15% iodixanol was selected as an optimal resin. Its initial compressive modulus of 10.9 kPa drops to 5.9 kPa after hyaluronidase treatment. This optically tuned photoresin enables fast VBP (23 s) of hydrogel constructs containing high densities (5×10^6/ml) of human mesenchymal stem cells (hMSCs) while retaining high viability and alkaline phosphatase activity in osteogenic culture. The bioprinted hydrogel constructs were subsequently digested by hyaluronidase, providing a softer matrix that enables faster and more pronounced cell spreading as well as enhanced expression of osteogenic biomarkers. Notably, hMSCs in the treated matrices formed a 3D cellular network on day 7. Deposition of hydroxyapatite mineral crystals in the construct was observed after 21 days of static tissue culture. Collectively, utilizing this optically tuned photoresin and enzymatic treatment presents a new methodology for fast fabrication of cm-scale 3D tissue models by photopolymerization-assisted VBP.



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THIOL-ENE POLYMERIZATION TOWARDS EASILY UP-SCALABLE GEL POLYMER ELECTROLYTE

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The continuous increase in energy consumption worldwide has catalysed the attention of both academy and industry on the production of safer and most efficient energy storage systems. The commonly employed Li-ion technology presents an intrinsic low safety due to the presence of liquid organic solvents which are prone to leakage and flammable, thus increasing the hazard risk upon battery short circuit. A simple solution to leakage is the employment of solid or semi-solid polymer electrolytes. Gel polymer electrolytes (GPEs) present the best compromise between mechanical and electrochemical properties, as well as an improvement of the cell safety [1]. The UV mediated radical polymerization is a common GPE fabrication strategy due to its speed and low cost. However, the polymerization can only start in the presence of an initiator, and it is hindered by oxygen, thus impeding the industrial scale up of the GPEs production. In this work, an UV mediated thiol-ene photopolymerization, employing polyethylene glycol diacrylate (PEGDA) and two different thiols (trimethylolpropane tris(3-mercaptopropionate) - T3 and pentaerythritol tetrakis(3-mercaptopropionate) - T4) as oligomer and crosslinkers, respectively, was carried out in a liquid electrolyte solution (1 M LiTFSI in EC/DEC) in order to obtain a self-standing GPE. The thiol-ene polymerization mechanism enable an easily up-scalable, fast, cheap and environmentally friendly GPE production, eliminating the need for a photoinitiator and an inert atmosphere [2]. A comparative study between the properties of membranes cured in an inert Ar atmosphere, as well as GPEs produced in a dry atmosphere, was performed. All the produced GPEs present an excellent room temperature ionic conductivity above 1 mS cm^{-2}, as well as a wide electrochemical stability window up to 4 V, demonstrating comparable properties when produced in presence or absence of oxygen and humidity. The full cells were tested to evaluate the rate capability of the GPEs comparing between membranes produced as self-standing and subsequently sandwiched between anode and cathode (referred to ex-situ), and GPEs directly cured on the cathode surface (referred to as in-situ).

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TUNEABLE LI-ION BATTERY SEPARATORS USING UV-INDUCED POLYMERIZATION-INDUCED PHASE SEPARATION

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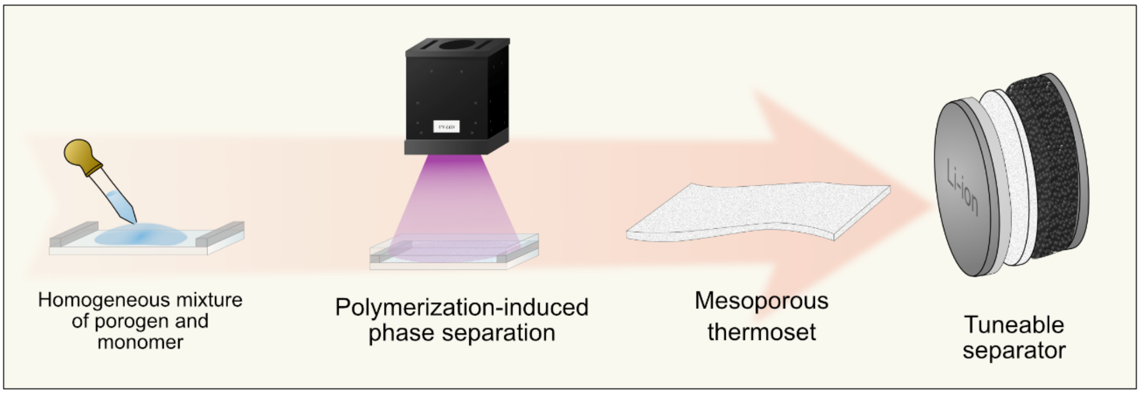
As we move to a carbon emissions-free society, batteries are becoming increasingly integral. An often-overlooked area of development within the battery research field is the separator. The current state-of-the-art in Li-ion batteries are polyolefin separators which are chemically inert and well proven at large production volumes. However, there is the potential to improve thermal and mechanical properties as well as enhancing dendrite suppression in new generation Lithium metal batteries.

Several approaches to develop advanced separators have been explored. For example, various coating techniques to enhance the properties of polyolefin separators have been developed. A variety of phase inversion and phase separation methods have also been demonstrated. [1] However, many of these procedures rely on several processing steps which increase the cost of the separator. An emerging alternative method is using polymerization-induced phase separation (PIPS), in which monomers are dissolved in porogenic solvents that phase separate upon UV-curing [2]. The result is a porous thermoset with both high mechanical and thermal stability. By varying the porogenic solvents and monomers, the microstructure is highly tuneable. In addition, the process is scalable, rapid, and energy efficient.

In this study, UV-initiated PIPS has been used to create mechanically robust separators using safe solvents. The structure-property relationship of the separators has been investigated, showing how different properties easily can be tuned. The cycling performance of the separators are also evaluated.

Vinnova via the Batteries Sweden Competence Center is acknowledged for funding this project.



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Towards more sustainable Li-O_2 batteries using bio-renewable organogels

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The growing need for clean energy production, due to global warming, has addressed the research towards the study of cleaner and more performing energy storage solutions and electric vehicles technologies. One of the most promising technologies currently being studied is the lithium - air battery, thanks to its high theoretical energy density of the order of 11000 Wh kg^{-1}. This extraordinary value is explained by the use of a metallic lithium anode but, above all, by the use of porous carbon cathodes (GDL) where the active material, oxygen, flows from the outside. The use of metallic lithium anodes, however, results in many drawbacks that limit the stability and cycling of these batteries. For this reason, in this work, two biorenewable organogel membranes have been studied for lithium protection.

The first membrane studied is based on gelatine from cold water fish skin. After a single step methacrylation in water, methacrylated gelatine is directly cross-linked in presence of liquid electrolyte through UV- initiated radical polymerization. The obtained gel polymer electrolytes present good thermal and mechanical properties, good electrochemical stability against Li metal and ionic conductivities as high as 2.51 mS cm^{-1} at room temperature. the Li-O_2 cells assembled with this bio-renewable gel polymer electrolytes were able to perform more than 100 cycles at 0.1 mA cm^{-2}, under constant O_2 flow, at room temperature and at a fixed capacity of 0.2 mAh cm^{-2}. Cathodes post- mortem analysis confirmed that the cross-linked gelatin matrix was able to slow down solvent degradation and therefore enhance the cell reversibility [1].

The second membrane studied is based on chitosan, a polysaccharide obtained from the deacetylation reaction of chitin. Once again, the methacrylation was performed through a simple, one-step reaction, in water, and the methacrylated chitosan was then cross-linked by UV induced radical polymerization. The obtained membranes were successively activated in liquid electrolyte (LiTFSI 0.5 M in DMSO) and used as lithium protection layer. The cells prepared with protected lithium were able to perform more than 40 cycles at 0.1 mA cm^{-2}, at a fixed capacity of 0.5 mAh cm^{-2}, under a constant O_2 flow of 4 ml min^{-1}, at room temperature, conserving 100 % coulombic efficiency. This is actually more than twice the lifespan of a similar cell containing bare metallic lithium, which failed in the same testing conditions, after 19 cycles [2].

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DEGRADATION OF MODIFIED POLYSTYRENES HAVING DEGRADABLE UNITS BY NEAR INFRARED LIGHT IRRADIATION

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Controlled degradation of polymers is getting more and more important to achieve a circular economy. The controlled degradation of polymers is effective against not only the reduction of polymeric waste but also the utilization of composite material products. Based on the degradation of composite material products, there are several reports based on the utilization of gas formation[1,2].

In this study, modified polystyrenes having tertiary ether linkages or carbonate linkages[3,4] were degraded by irradiation of near infrared light (NIR) and subsequent heating. The polymer films containing a photoacid generator[5] and commercially-available photon upconversion nanoparticles (UCNPs)[6] were decomposed to form isobutene and/or carbon dioxide by NIR irradiation and subsequent heating. The thermal decomposition behaviors of the polymers were investigated and discussed in terms of the chemical structures of the degradable units.

Poly(*p*-*tert*-butoxycarbonyloxystyrene) (PBOCS) and poly(*p*-*tert*-butoxystyrene) (PTBOS) having tertiary ether linkages or carbonate linkages were degraded by NIR (810 nm) irradiation and subsequent heating. The polymer films containing PAG1 and UCNP were decomposed to form isobutene and/or carbon dioxide by NIR irradiation and subsequent heating. The optimum degradation conditions were as follows: 90-min NIR irradiation and baked at 160 °C for 5 min (PBOCS), 120-min NIR irradiation and baked at 140 °C for 5 min (PTBOS). We believe that PTBOS is a promising candidate as a degradable polymer due to its high thermal stability by the NIR degradation and subsequent heating which contributes to easy recycling of composite materials.

This study was supported by a Grant-in-Aid by JST, CREST Grant Number JPMJCR21L3, Japan. The authors would like to thank Prof. Bernd Strehmel for the useful discussion of NIR irradiation, Assoc. Prof. Yasunori Matsui and Prof. Hiroshi Ikeda, Osaka Metropolitan University, for measurements of the fluorescence spectra of UCNP, and Dr. Hideki Tachi, Osaka Research Institute of Industrial Science and Technology, for measurements of FE-SEM.

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PHOTOCAGED AMINES AS BASE CATALYSTS FOR RING-OPENING POLYMERIZATION OF *N*-CARBOXYANHYDRIDES

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Ring-opening polymerization (ROP) of *N*-carboxyanhydrides (NCAs) has attracted considerable attention as a means to prepare synthetic polypeptides with tunable molecular weight and chemical structure, and the ability to incorporate different functional groups into the polymer. The use of light to spatially and temporally control the ROP of NCAs could expand the applicability of synthetic polypeptides, including in the field of additive manufacturing.

In this work, we investigate the photoinduced ROP of γ-benzyl-L-glutamate (BLG) NCA using various photocaged amines (photobases) as catalysts (Figure 1), using members from two distinct groups, i.e., i) ammonium salts and ii) carbamate photobases. When irradiated with light at 365 nm, the photobases are photolyzed and the amines are released, acting as a base. We have shown that the photoreleased amines can trigger the polymerization of BLG NCA and that the polymerization process is influenced by the choice of photobase. Furthermore, the ROP of BLG NCA catalysed by an uncaged amine differs from that of the corresponding free amine in the polymerization rate and molecular weight characteristics of the obtained polypeptide, as confirmed by ^{1}H NMR and FTIR spectroscopies and SEC.

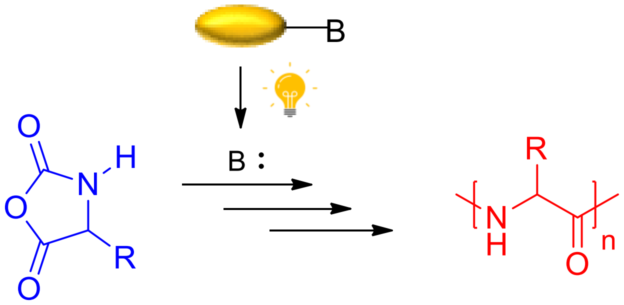

Figure 1: Photoinduced ROP of NCA monomers catalysed by a photoreleased base.

3D Printable Photocurable Polymers and Terahertz: A Pathway to Next-Generation Devices for 6G Technologies.

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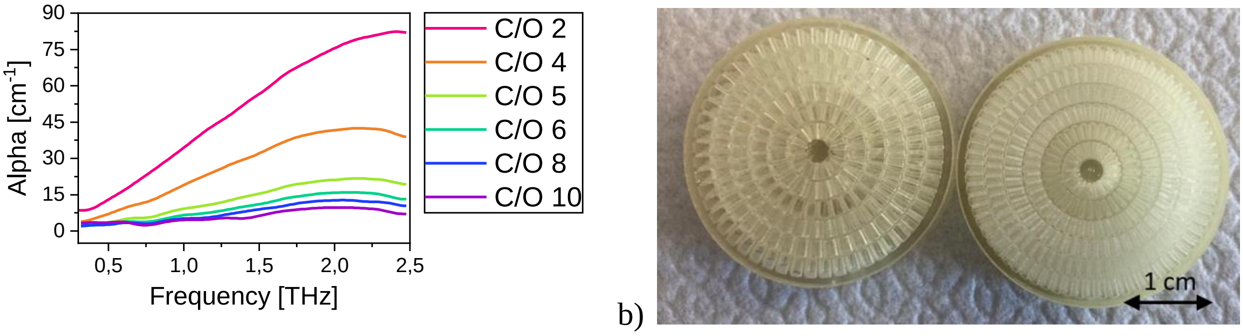
The next generation of wireless communication (6G), foreseen for the 2030s, will be based on terahertz (THz) radiation. 6G is predicted to aggregate multiple types of resources, becoming a digital ecosystem that connects the digital, physical, and human worlds.[1] To achieve this goal, it is thus necessary to minimize the existing gap between cyber and physical worlds, with distributed and adaptive interactions between THz and devices. Beyond 6G, THz frequencies are also gaining interest for many applications in different areas such as biomedical, quality control, security, and defense.[2]

Despite the pivotal role that this part of the electromagnetic spectrum will play in the next future, the knowledge on matter/radiation interaction is lacking, especially for polymeric materials. To address this, experiments on various photocured polymers with different chemical compositions were conducted to understand the relationship between their chemical structure and THz absorption. The materials studied were photocured acrylates, methacrylates, and thiol-ene resins, selected because of the easy tailoring of chemical and physical characteristics by changing the ingredients of the photocurable formulations.[3] In particular, the impact on THz absorption of materials with different chemical components in their molecular structure was assessed. The analyses evidenced a precise relationship between chemical structure and THz interaction, allowing control of THz transparency (Fig. 1a). The definition of this dataset was the cornerstone for the next step, which was the development of devices with user-defined properties. A key-approach is the fabrication of metamaterials, objects in which materials properties and object design play a synergistic role, defining tunable absorbance properties. To obtain this unique interaction, for THz-metamaterials, geometric features of hundreds of microns are necessary. Those characteristics are perfectly compatible with 3D printing capabilities, in particular with Digital Light Processing (DLP) technology (Fig. 1b). Here, Metamaterials were designed using simulation tools and then fabricated via DLP 3D Printing.



a) b)

Figure 1. a) Absorption coefficient of photocured polymers with different carbon content; b) example of DLP 3D printed object.

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1,2-Dithiolanes as Building Blocks to Intrinsically High Refractive Index Polymers

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With the pursuit advances in optical devices the need for high refractive index, high thermal stability, high transparency, and low birefringence polymers have increased substantially. A typical strategy to develop high refractive index polymers is the incorporation of high molar fraction groups such as sulfur, phosphorous, bromine, iodine and/or aromatic structures. Due to its high polarizability, high stability, and straightforward insertion in its molecular structure sulfur is one of the elements most commonly use to increase the refractive index of polymers. A particular class of sulfur-containing molecules 1,2-dithiolanes, which contain a saturated five-membered disulfide ring, shown remarkable potential for the development of intrinsically high refractive index polymers with low volumetric shrinkage, due to its ability to participate in a variety of radical and ionic ring opening reactions yielding thiolate or sulfur-centered radicals each of which can initiate ring opening oligomerization or polymerization with another cyclic disulfide producing disulfide-rich backbone of poly(dithiolane)s.[1,2] Among the 1,2-dithiolanes molecules, lipoic and asparagusic acid (natural occurring molecules) are perhaps the best-known members of this group. The ring opening reaction of 1,2 dithiolanes occur via both thermally and light mediated polymerizations even in the absence of initiator.[3] In this paper, we present a new framework for the preparation of intrinsically high refractive index (HRIPs).

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PHOTOSENSITIVE COVALENT ADAPTABLE NETWORKS FOR SURFACE FEATURES

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Abstract

Covalent adaptable networks (CANs), are thermoset polymers that incorporate dynamic covalent bonds to allow for the rearrangement of network topology, therefore enabling processes including stress relaxation, self-healing, and recycling. Photoresponsive dynamic moieties, such as allyl sulfides, enable spaciotemporal control over these effects. Kloxin et al. leveraged this feature to pattern surface topology by applying strain to elastomeric networks and subsequently activating localized stress relaxation, therefore thinning the region of interest.[1] This work builds on the mechanophotopattering process by developing methods for controlling the properties and patterns of smaller features than previously explored. Specifically, seeking to understand the analogue response of surface features to discreetly control size and structure; thereby enabling the production of complex and precise topographical designs.

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SONICATION LABILE PHOTCHEMICALLY CROSSLINKED POLYMERS

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In the growing field of polymers, the development of materials that are responsive to external stimuli has gained momentum, especially with the interest in enabling transitions of mechanical or chemical properties to allow a single polymer to be used where previously multiple may have been required. This work integrates mechanophore moieties into polymers to facilitate a mechanical response. A phthalaldehyde moiety is built into polyethylene glycol (PEG) macromers endcapped with reactive alkenes and the macromer is then photochemically crosslinked to synthesize hydrogels that degrade in response to a mechanical trigger, probe sonication. The degradation and subsequent breakdown of the network into soluble byproducts is characterized through rheology, mass loss, and GPC as sonication is applied to the system. The use of mechanical triggers, such as sonication or ultrasound, was leveraged to degrade polymers in optically dense or thermally sensitive environments while maintaining the spatial – temporal control characteristic of photo triggered degradation mechanisms.

Chemical and Physical Drying of Coatings between 750–1050 nm: Replacement of furnace technologies

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NIR absorbers based on functionalized polymetines possess the potential to replace older oven techniques by a photonic source namely a high-power NIR LED emitting between 700-1100 nm. These materials facilitate conversion of absorbed light energy into heat as the main component. Therefore, combination of them with NIR sources facilitates film formation of processed coatings on a selected substrate. High power NIR-LEDs have appeared on the scene as their use offers many advantages over corresponding NIR lasers. This work preferably focuses on LEDs emitting at 860 nm, 940 nm or 1050 nm.

There exists a relationship between the structural pattern of the cyanine absorber and generation non-radiative deactivation as main channel to generate heat. Internal conversion proceeding between the lowest vibrational mode of the excited state and a higher vibrational mode of the ground state explains the scenario. Collision of such a hot molecule with matrix molecules fundaments the main process contributing to heat generation. Generated temperature can reach several hundred Celsius degrees. This technology works well even on temperature-sensitive substrates since light absorption and heat generation take place mainly in the coating with high selectivity.

NIR absorbers comprising benzo[c,d]- or benzo[e]indolium pattern absorb between 800-1100 nm with extinction coefficients of several 10^5 $M^{-1}cm^{-1}$. An example shows thermal initiation of a chemical reaction leading to formation of a polyurethane comprising a blocked isocyanate. Temperature generated results in formation of the isocyanate >180°C. This new type of photopolymerization leads to crosslinking.

Compatibility of the absorber, controlled by the molecular pattern of the absorber at different positions, with the matrix can be seen as a further important parameter. Aggregation should be therefore avoided. Photonic drying of coating systems offers the great advantage that the heat required for solidification penetrates directly into the place where it would be needed on demand.

INNOVATIVE ELECTROSPUN NANOFIBER MEMBRANE BY COUPLING ELECTROSPINNING AND PHOTOINDUCED PROCESS

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Electrospinning is well-known as a versatile technique for generating fibers down to the nanoscale and has emerged as a prominent technique with widespread application[1]. Electrospun nanofiber membranes (ENMs) are candidates for water purification due to their exceptional properties, including large surface area, high porosity, adjustable pore structure, which surpass current conventional materials and techniques[2]. Further, photo-crosslinking can be employed to improve the thermal, mechanical, and solvent resistance of the membranes, and the photoinduced process can also impart or augment specific functionalities to ENMs[3].

In this study, electrospinning of styrene-butadiene rubber latexes (thus using only water as a solvent to mitigate environmental and human concerns) and subsequent thiol-ene photoinduced crosslinking are studied. The influence of polymer suspension properties, electrospinning conditions, and photo-crosslinking parameters and conditions are assessed to tailor the final properties of the ENMs. The resulting electrospun nanofiber membranes will be evaluated in a wide range of applications, including water treatment for heavy metal removal.

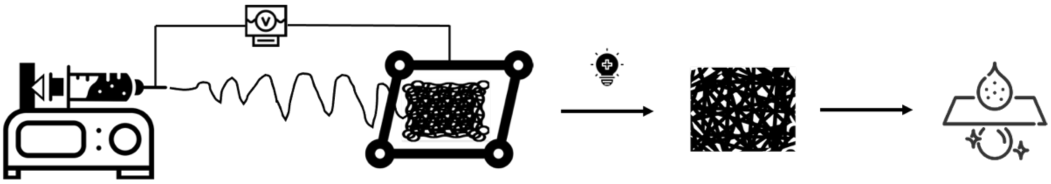

Figure 1. A multi-step and multi-scale approach for generating functional ENMs for water treatment

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ESPERANTO Enhancing the Sustainability of PhotopolymERs ANd phoToinduced prOcesses

Funded by the European Union

EVALUATION OF VARIOUS MONOFUNCTIONAL MONOMERS FOR THE DEVELOPMENT OF FRACTURE TOUGH DENTAL MATERIALS CONTAINING AN ABA TRIBLOCK COPOLYMER

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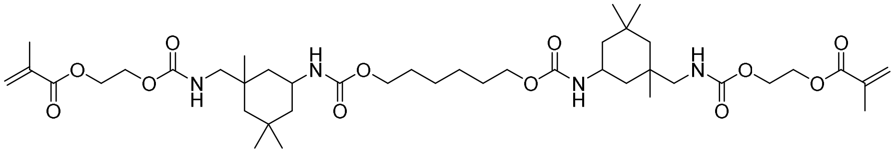
The additive manufacturing of dental protheses by 3D printing requires the formation of materials with excellent mechanical properties and a high fracture toughness. While the applicability of common monofunctional (meth)acrylate monomers in 3D printing is limited due to their low reactivity and high volatility, resins consisting predominantly of multifunctional (meth)acrylates usually result in brittle materials with a high crosslinking density, which are not suitable for the preparation of dentures. Materials with a moderate crosslinking density can be obtained from mixtures of mono- and multifunctional monomers. The addition of block copolymers (BCP) as toughening agents to those resins can significantly improve the fracture toughness of the resulting cured materials.[1]

In order to assess the impact of the monofunctional monomer on the mechanical performance of the resulting materials, the urethane dimethacrylate crosslinker **DMA1** was combined with several monofunctional (meth)acrylates, and a PCL-*b*-PDMS-*b*-PCL triblock copolymer was added as a toughener. The influence of the nature of the monofunctional monomer as well as the concentration of the BCP on fracture toughness, flexural strength and flexural modulus of the cured materials was investigated.



DMA1

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ANALYSIS OF THE POTENTIAL FOR INTEGRATION OF LOW TEMPERATURE SOLAR THERMAL ENERGY SYSTEMS IN POLYMER PROCESSING CHAINS

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Polymer processing requires large amounts of energy, usually in the form of electricity for heat generation. Reducing this primary energy demand has been shown to be the best strategy for mitigating the industry's impact on global energy needs [1]. One alternative to achieve such a reduction is the incorporation of solar thermal technologies at different stages of plastics processing [2]. Currently, almost all low- and medium-temperature solar thermal collectors can reach temperatures above the melting points of most industrial polymers. For this reason, the present work explores the possibility of partially replacing thermal energy consumption in a plant producing flexible pipe for crop irrigation from recycled polyethylene in Bucaramanga, Colombia. TRNSYS software was used to simulate the performance of a solar thermal energy system (STES) integrated in the drying stage of the material and as preheating prior to extrusion. The energy demand was estimated using both secondary and primary data obtained in a production plant. The solar thermal irradiance data set was obtained from the analysis of the information reported in different databases for the area under study. The technical parameters of the STES were obtained from secondary data, complemented with the performance analysis of a solar heating system implemented in previous research. The use of concentrating and non-concentrating solar thermal collectors was evaluated, while for the final use of heat, it was proposed the utilization of continuous furnaces in order to avoid the energy cost of heating air, as has been reported in the literature [3]. Preliminary results show that it is possible to replace between 5% and 10% of the thermal energy demands for the company's current production volume, the main constraint being the high-power levels required. Although the use of concentrating collectors allows easily reaching higher temperatures than non-concentrating ones, both allow working above the melting temperature of polyethylene, so that economic and logistic factors should be considered when making decisions. Likewise, the results allow us to conclude that by increasing the scale of application of the technology and the thermal energy production capacity, it would be possible to consider the design of facilities that operate with almost all their heat demand supplied from solar thermal energy. Authors would like to thank The Royal Society for supporting this research through the Enabling Harvesting of Solar Energy for Remote Applications in the Andes Region (LA-SOLAR ENHANCE- ICA\R1\191201) project.

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Exploiting Me-β-Cyclodextrin Host-Guest Complexation for Obtaining Water-Borne UV-Curable Coatings

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Cyclodextrins are a category of cyclic oligosaccharides constituted by 6, 7 or 8 glucopyranose units linked together by α-1,4 bonds, obtaining a toroidal structure that will be called α-CD, β-CD or γ-CD, respectively[1-3]. This molecular structure defines the presence of a cavity characterised by not only a specific diameter and size, but also by an amphiphilic behaviour. In fact, while the outside is hydrophilic due to the presence of hydroxyl groups, the inside is hydrophobic, so the latter could receive organic guest molecules in order to form water-soluble inclusion complexes[3-4]. This characteristic, together with other advantages such as low toxicity, high biodegradability, biocompatibility, versatility and availability[2], make this family of compounds eligible to be used in the production of UV-curable polymers. In fact, the advantages of the cyclodextrins could be combined with the low VOC emissions, high efficiency and low energy consumption of the UV curing process in order to produce polymeric materials such as coatings, adhesives and inks in a more environmentally friendly way[5]. This study focuses on the utilization of a Me-β-CD derivative for complexing oil-soluble monomers and photoinitiators in water, aiming to achieve UV-cured coatings with adjustable mechanical and optical properties.

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