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## BIOCOMPATIBLE PHOTOPOLYMER COMPOSITES FOR POTENTIAL BONE REPLACEMENTS

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The market for bio implants was worth 94.1 billion worldwide and is expected to grow 7.3% until 2017<sup>1</sup> due to increase of chronic bone and joint diseases. Development/Improvement of biomaterials and processing techniques is inseparably related with this field. In current Regenerative Medicine and Tissue Engineering temporary scaffolds are used to provide mechanical and structural stability to replace/support the damaged tissue and also mimic the extracellular matrix helping cells to attach and proliferate. The scaffold should then degrade into non-toxic products that can be easily transported out of the system.

We investigated the application of Additive Manufacturing Technologies using photopolymerizable Thiol-Ene systems to create such biodegradable scaffolds. To avoid acrylates and methacrylates, due to cytotoxicity<sup>2</sup>, different divinyl esters were synthesized as Ene-component. Three trifunctional thiols with molecular weights from 400-1300 g<sup>\*</sup>mol<sup>-1</sup> were used. The resins were filled with tricalciumphosphate (TCP) to further enhance the mechanical properties. Lithography-based Ceramic Manufacturing (LCM) was the method of choice for 3D printing.

Besides divinyl adipate, which is the only commercially available divinyl ester, the divinyl esters were synthesized by transesterification reaction with Lipase *Candida Antarctica* (CAL-B). The transesterification could be carried out without additional solvent in 2 of 3 cases. Conversion yields were good and up-scaling was successful. Three different spacers were used to cover a broad range of mechanical properties and degradation behavior. Photoreactivity was analyzed by Photo DSC measurements of the pure divinyl esters and mixtures with all trithiols. Photorheology measurements were done to determine which mixtures are suitable for 3D printing. The curing process could be followed by simultaneous IR- and rheology measurements. Selected mixtures were filled with TCP and printed using the LCM technology. Mechanical testing, such as 3 Point Bending, Nanoindentation and DMA, was performed on the printed specimens. Meanwhile the degradation behavior of cured pellets from selected mixtures in phosphate buffered saline (PBS) was investigated.

### Conclusions

Divinyl esters are a good substitute for acrylates and methacrylates as basis for bio-implants. With the advantages of Thiol-Ene chemistry the lower reactivity of vinyl esters can be compensated. Photo DSC measurements showed that the added thiols significantly boost the reactivity of the systems. It is also known, that thiols reduce oxygen inhibition in photopolymerization. With different spacers we were able to tune degradation behavior as well as the mechanical properties. We also proved that LCM is a suitable technique to process these resins and realize the desired scaffolds.

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## HYDROTHERMAL POLYMERIZATION: TOWARDS HIGHLY CRYSTALLINE HIGH-PERFORMANCE POLYMERS

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Hydrothermal polymerization (HTP) is a novel synthetic approach for conceiving highly crystalline condensation polymers.<sup>1</sup> The technique is geomimetic, *i.e.* inspired by geological ore formation: numerous minerals crystallize in so-called hydrothermal veins. Natural zeolites are for instance exclusively of hydrothermal origin.<sup>2</sup> The formation of silicates from silicic acid species is, mechanistically speaking, a polycondensation with elimination of the byproduct water. The formation of several organic condensation polymers is closely related: for instance polyimides are generated by condensation of amine with  $\alpha,\beta$ -dicarboxylic acid functions to imide moieties by elimination of H<sub>2</sub>O. We could recently show that polyimides can be obtained hydrothermally with outstanding crystallinity.<sup>1</sup>

Hydrothermal conditions are mimicked in the laboratory by using autoclaves, in which the monomers and water are enclosed. By heating up the autoclave to temperatures > 100 °C the respective autogenous pressure (> 1 bar) builds up and the reaction mixture thus reaches the hydrothermal regime.

In this contribution, we present a global picture of HTP, which addresses the following questions: (i) Why does HTP yield crystalline products while classical PI syntheses do not? (ii) What are the mechanistic ongoings during HTP? (iii) How do the reaction parameters influence the final PI product (*e.g.* final crystallinity, morphology)?

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## POSTMODIFICATION OF EPOXYFUNCTIONALIZED POLYOLEFINES

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### Introduction

Polyolefines have an outstanding chemical inertness. Therefore the most chemical post-polymerization modification techniques are rather harsh methods and lead to unspecific introduction of polar groups. Free radical grafting is one of only a few methods available to covalently bond specific reactive groups (e.g. epoxy groups) to polyolefins, and make it therefore accessible for further modifications<sup>1,2</sup>. Such second stage modifications are the aim of our work and we investigated which features a NIR absorber must have to be efficiently bonded to epoxy functionalized polypropylene. A covalently bonded NIR absorber that is homogeneously spread in polypropylene and stays there even though the NIR absorber is more polar than its host material would have many applications e.g. in the field of laser welding and cutting<sup>3</sup>. These techniques use NIR-Laser (Diode, NdYAG, CO<sub>2</sub> laser) to bring the necessary thermal energy in the material. Due to the fact that polypropylene is rather IR transparent, NIR-absorbers like graphite, nanomaterials or organic dyes, are needed. These additives tend to cause problems like separation, agglomeration or migration, especially in a very non polar environment.

### Results and Discussion

A screening with a Simultaneous Thermal Analysis apparatus was done to investigate the reactivity of different moieties toward epoxy groups under thermal conditions similar to those found in an extruder. Therefore different (model) substances were used for the epoxy site (see Figure 1) as well as for the "attacking" site (different aromatic and aliphatic amines and carboxylic acids). The results were compared and aligned with those from analytical studies of the reaction products (e.g. FTIR) and ab initio calculations of the theoretical reaction enthalpies to gain information to design a NIR absorber which fits the requirements for a second stage modification of melt grafted polypropylene.

The chromophor of the NIR absorber (see Figure 2) was synthesized via five steps, and it was possible to implement some remarkable improvements compared to the literature methods<sup>4</sup>.

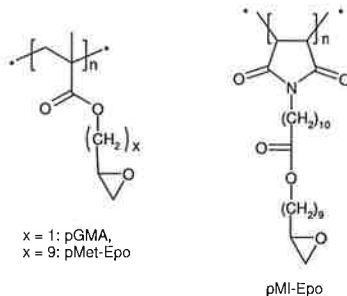


Figure 1: Used epoxy homopolymers

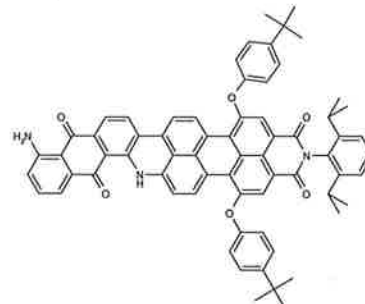


Figure 2: Synthesised NIR absorber

Characterization of the NIR absorber will be presented and discussed as well as an outlook for further promising optimization possibilities.

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## RIGID POLYURETHANE FOAMS FROM TAILORED LIGNIN POLYOLS

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### Introduction

Polyurethane (PU) foams are widely used in various applications due to their ease of processing and excellent thermal insulation properties. Conventional PU foams are based on hydroxyl terminated polyethers or polyesters and isocyanates, hence on raw materials mainly obtained from fossil fuel resources. Due to the increasing concern about the shortage of fossil fuels, synthesis of polyols from renewable biomass resources has been a focus in the polyurethane research during the last decade.<sup>1</sup>

Lignin, the second major component of wood and annual plants, is available in huge quantities due to the pulp and paper industry and lignocellulosic biorefineries. Until now only seen as a cheap low-value by-product, it still has potential to replace conventional petroleum-based polyols in PU foams. A promising method to tailor lignin's properties regarding hydroxyl number and viscosity is liquefaction by oxyalkylation.<sup>2</sup>

### Experimental

Lignin was reacted with propylene oxide (PO) and ethylene oxide (EO), respectively, under alkaline catalysis. The ratio of PO or EO to lignin was varied and thus polyols with different viscosities and hydroxyl numbers were obtained.

PU foams were prepared by mixing the most promising polyols with surfactant, catalyst and blowing agent (water and pentane, respectively) and adding polymeric methylene diphenyl diisocyanate.

Thermal properties were obtained by differential scanning calorimetry, thermal gravimetric analysis as well as thermal conductivity measurements. Morphology was studied by scanning electron microscopy and also compression strength was tested.

### Results and Discussion

Suitable lignin polyols had hydroxyl numbers in the range from 100-500 mg KOH/g and viscosities below 300 Pa·s. It turned out that pentane is not qualified as blowing agent for formulations containing oxyethylated lignins whereas oxypropylated lignins can be used with both blowing agents.

The SEM images revealed that pentane-blown foams show a honeycomb structure with closed cells, while water-blown foams have, as expected, an open-cell structure. Water-blown-foams had a slightly higher thermal conductivity than pentane-blown foams, whose values are in the range of the non-lignin pentane-blown control foam. Most foams showed thermal stability up to 200 °C and performed well in compression strength tests.

### Conclusions

Rigid polyurethane foams were successfully synthesized from oxyalkylated lignin. Pentane-blown foams of lignopolyols are suitable for the application as insulating material. The water-blown foams had higher thermal conductivities due to their open-cell structure.

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1. Zheng, Z., et al., Bio-based rigid polyurethane foam from liquefied products of wood in the presence of polyhydric alcohols, *Advanced Materials Research*, 2011, 168-170, 1281-1284.
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## HYALURONIC ACID BASED HYDROGELS FOR TWO PHOTON LITHOGRAPHY

ZUZANA TOMÁŠIKOVÁ<sup>a)</sup>, BRANISLAV HUSÁR<sup>a)</sup>, XIAO-HUA QIN<sup>a)</sup>, PETER GRUBER<sup>b)</sup>, MARICA MARKOVIC<sup>b)</sup>, ALEKSANDR OVSIANIKOV<sup>b)</sup>, ROBERT LISKA<sup>a)</sup>

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Hydrogels are crosslinked polymer networks with the affinity to swell in aqueous media. The increasing usage of these materials especially in biomedical field can be referred back to the properties in mimicking extracellular matrix such as high water content or oxygen permeability. Due to the corresponding mechanical properties the applications find place especially in soft tissue regeneration and/or replacement, such as skin or cartilage repair. The microstructure of the native tissue offers mechanical support in form of scaffolds, on which cells can attach and proliferate. The porosity allows cell migration as well as transport of the nutrients and metabolic waste products. Regarding the structural complexity of the native tissues, fabrication methods of high accuracy and high resolution are demanded. One of the possible fabrication methods for 3D structures is photopolymerization, where light of specific wavelength is used to cure the precursors and form (hydro-)gels. Two photon lithography (also known as two photon polymerization, 2PP) is a special case of photopolymerization and allows high resolution 3D writing in liquid precursor formulation using NIR laser<sup>1</sup>. User defined 3D scaffolds with a high complexity can be obtained. The need of photopolymerizable and reactive precursors, such as acrylates, is therefore necessary. Unfortunately acrylates often act irritant or cytotoxic<sup>2</sup> and therefore a more biocompatible alternative has to be found for applications in tissue engineering. Synthesis of novel photopolymerizable precursors based on hyaluronic acid was performed by enzymatic transesterification. Their cytotoxicity in solution as well as their reactivity via photorheology were investigated. Vinyl esters perform better in terms of biocompatibility as their acrylic counterparts<sup>2</sup>. Swelling behavior and mechanical properties of the hyaluronic acid vinyl esters (HAVE) hydrogels were also tested and compared to the acrylate based reference. The suboptimal reactivity of HAVE in comparison to acrylates can be increased by using thiols. Different substitution degrees on vinyl esters induce tunable crosslinking densities in the final material, which allows formation of hydrogels with tunable mechanical properties. HAVE formulations were successfully used to print 3D structure as well as to encapsulate cells by 2PP.

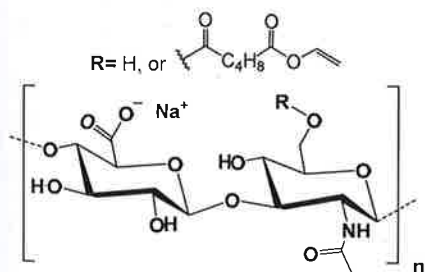


Figure 1: Hyaluronan vinyl ester (HAVE)



Figure 2: HAVE hydrogel printed by 2PP

### References:

- Ovsianikov A., Mironov V., Stampfl J., Liska R.: Engineering 3D cell-culture matrices: multiphoton processing technologies for biological and tissue engineering applications, *Expert Review of Medical Devices*, 2012, 9, 613 - 633
- Heller C., Schwentenwein M., Russmueller G., Varga F., Stampfl J., Liska R.: Vinyl esters: Low cytotoxicity monomers for the fabrication of biocompatible 3D scaffolds by lithography based additive manufacturing, *J. Polym. Sci., Part A: Polym. Chem.*, 2009, 47, 24, 6941-6954

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Hydrogels are crosslinked polymer networks with the affinity to swell in aqueous media. The increasing usage of these materials especially in biomedical field can be referred back to the properties in mimicking extracellular matrix such as high water content or oxygen permeability. Due to the corresponding mechanical properties the applications find place especially in soft tissue regeneration and/or replacement, such as skin or cartilage repair. The microstructure of the native tissue offers mechanical support in form of scaffolds, on which cells can attach and proliferate. The porosity allows cell migration as well as transport of the nutrients and metabolic waste products. Regarding the structural complexity of the native tissues, fabrication methods of high accuracy and high resolution are demanded. One of the possible fabrication methods for 3D structures is photopolymerization, where light of specific wavelength is used to cure the precursors and form (hydro-)gels. Two photon lithography (also known as two photon polymerization, 2PP) is a special case of photopolymerization and allows high resolution 3D writing in liquid precursor formulation using NIR laser<sup>1</sup>. User defined 3D scaffolds with a high complexity can be obtained. The need of photopolymerizable and reactive precursors, such as acrylates, is therefore necessary. Unfortunately acrylates often act irritant or cytotoxic<sup>2</sup> and therefore a more biocompatible alternative has to be found for applications in tissue engineering. Synthesis of novel photopolymerizable precursors based on hyaluronic acid was performed by enzymatic transesterification. Their cytotoxicity in solution as well as their reactivity via photorheology were investigated. Vinyl esters perform better in terms of biocompatibility as their acrylic counterparts<sup>2</sup>. Swelling behavior and mechanical properties of the hyaluronic acid vinyl esters (HAVE) hydrogels were also tested and compared to the acrylate based reference. The suboptimal reactivity of HAVE in comparison to acrylates can be increased by using thiols. Different substitution degrees on vinyl esters induce tunable crosslinking densities in the final material, which allows formation of hydrogels with tunable mechanical properties. HAVE formulations were successfully used to print 3D structure as well as to encapsulate cells by 2PP.

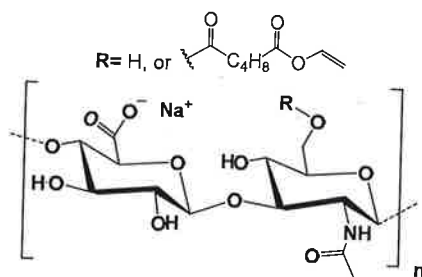


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## CATIONIC FRONTAL POLYMERIZATION FOR THE PRODUCTION OF ELECTRICAL INSULATING MATERIALS

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For electrical insulation e.g. in HV generators, composite insulations based on mica and epoxy resins are frequently employed. A common way to obtain such insulations is the impregnation of mica tapes that are wound around Roebel bars with liquid epoxy resins followed by thermal curing in an oven. In conventional systems, the epoxy component (e.g. DGEBA) is cured with an anhydride in the presence of a catalyst to give a duromer containing ester groups. Whilst this process is well established in electrical industry, a drawback is the long curing time at elevated temperatures and the high energy consumption of the whole curing process.

With a technique called frontal polymerization we aim to circumvent this disadvantage. Instead of the addition of anhydride based hardeners a cationic photo initiator in combination with a radical thermal initiator is added to the epoxy component. This formulation is capable of producing a reaction front that is self-sustained by the produced reaction-heat and after initiation it moves along until the whole formulation is cured.

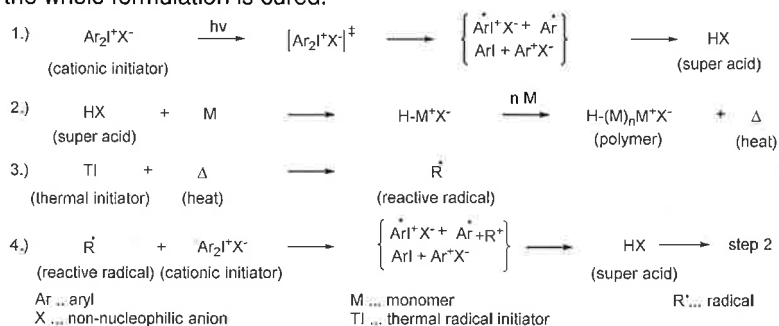


Figure 1 Scheme of the radical induced cationic frontal polymerization of an epoxide

Figure 1 shows the reaction process of such a radical induced cationic frontal polymerization. In the first step a cationic photo acid is generated by the irradiation of an arylidonium salt. This photoacid polymerizes the epoxide and generates polymerization heat which will in the next step cleave the thermal initiator resulting in the formation of reactive radicals. In the last step these generated radicals can react with the arylidonium salt and cleave it even without any further light irradiation. This leads again to the formation of a photoacid which will polymerize the epoxy resin formulation to give a polyether network (step 2 in Fig.1).

This process will keep itself alive until (1) the amount of heat dissipated is larger than the amount of heat produced and therefore will lower the temperature below a certain level that is needed for the cleavage of the thermal initiator or (2) until the whole formulation has been cured. Figure 2 shows a scheme of a light induced frontal polymerization.

With this process the energy consumption of the curing process can be significantly lowered and also the time needed for the polymerization process is reduced from many hours to a few minutes.

**Acknowledgement:** This research has been performed within the K-project "PolyComp". Funding by the Austrian Research Promotion Agency (FFG) is gratefully acknowledged.

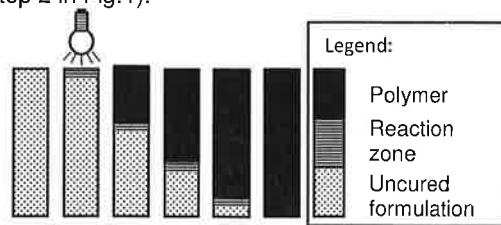


Figure 2: Scheme of a photo-induced frontal polymerization



## THE INFLUENCE OF ADDITION-FRAGMENTATION-CHAIN-TRANSFER ON MECHANICAL PROPERTIES OF METHACRYLATE NETWORKS

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Photo induced radical polymerization is for years a commonly used method in a broad field of applications like coatings and in dentistry.

In free-radical polymerization processes three-dimensional networks are formed. These networks have to fulfill a variety of requirements including high reactivity and low toxicity of the monomers and also good mechanical properties like high strength, stiffness and low brittleness.

The formed networks are inhomogeneous and are characterized by poor mechanical properties of the resulting polymer, especially low toughness. To overcome this drawback, chain transfer agents (CTAs) which regulate the polymer network can be used. These CTAs turn the chain-growth polymerization into a mixed chain-step-growth polymerization, which leads to lower shrinkage stress and better mechanical properties. Typically in literature used CTAs are thiols but they have disadvantages, for example their odor<sup>1</sup> and the poor storage stability of the formulations. Next to thiols there is a wide variety of potential CTAs, which can be used to regulate such network. A good overview thereof is given by Moad et al.<sup>2</sup>

The aim of this work was the controlled polymerization of dimethacrylates based on the usage of CTAs. Therefore, different types of CTAs based on the methacrylate lead structure were synthesized. These CTAs were used in order to generate regulated polymer networks with preferably improved mechanical properties compared to networks formed without CTAs.

Mechanical properties and retardation were determined in a dimethacrylate matrix with DMTA, Photo-DSC, Photo-Rheology-IR-Coupling and Dynstat Test.

Summing up, the goal was successfully achieved, as regulated polymer networks with an up to sevenfold increase in impact resistance were obtained. Furthermore, their shrinkage stress could be reduced up to a maximum of 50 percent.

**Acknowledgement:** We want to thank the Christian Doppler Society for the financial support.

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## BENZOYL PHENYLTELLURIDE AS HIGHLY REACTIVE TERP-REAGENT FOR VISIBLE LIGHT INDUCED CONTROLLED RADICAL POLYMERIZATION

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### Abstract

Benzoyl phenyltelluride (**BPT**) is a compound, which is able to induce controlled radical polymerization with a visible light (400-500 nm) radiation source. It can be easily synthesized in one step from diphenyl ditelluride and benzoyl chloride and belongs to a class of compounds called TERP-reagents (Tellurium Mediated Controlled radical Polymerization), which basically all provide similar features. However, the outstanding characteristic of our compound is the ability to efficiently induce and propagate polymerization without additional thermal initiator and at room temperature.

**BPT** shows a strong absorption maximum at 407 nm that tails out to 473 nm. The achievable PDIs (1.2-1.3) are among the lowest reported in literature for light induced controlled radical polymerization. Photoinitiators are at present state of the art when it comes to this technology. In comparison to photoinitiators **BPT** shows its full potential. PDIs obtained with **BPT** are much lower than for example those for benzyl dithiocarbamate (**BDC**) (1.7-1.8), which was used as a reference compound.

**BDC** was used as reference because of its property as UV-photoinitiator and its similar initiation/control mechanism. However, in contrast to our compound **BPT**, **BDC** does not allow living radical polymerization under visible light.

**BPT** can be used for polymerization of acrylamides and acrylates (Figure 1). Photoinitiation of styrene was not possible and with methacrylates no living radical polymerization was achieved.

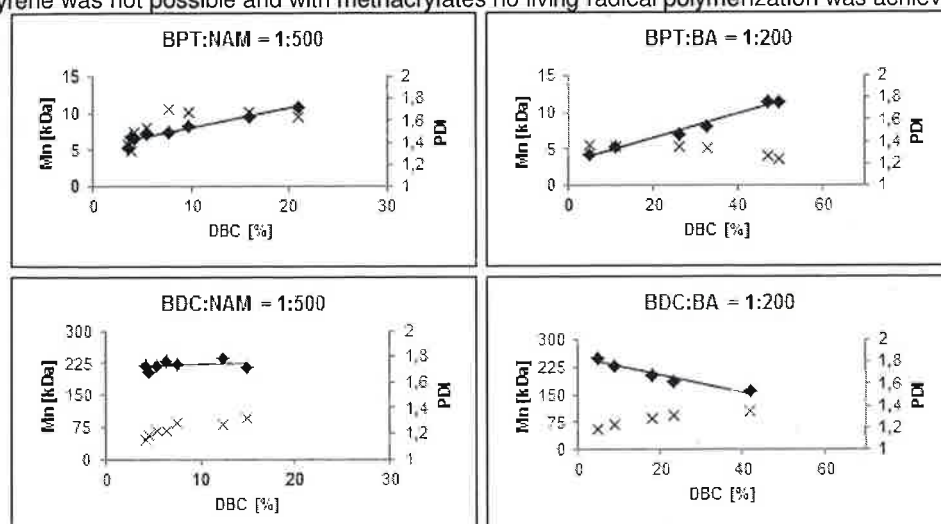


Figure 1: Kinetic data of polymerization with our **BPT** and the reference **BDC** under visible light (400-500 nm) and with butylacrylate (BA) and 4-acryloylmorpholine (NAM) as monomers.

**Acknowledgement:** We thank the Christian Doppler Society for financial support.

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Benedikt, S., Moszner, N. and Liska, R., Benzoyl Phenyltelluride as Highly Reactive Visible-Light TERP-Reagent for Controlled Radical Polymerization, *Macromolecules* (Washington, DC, U. S.), 2014, 47(16), 5526-5531.

## SYNTHESIS OF AMPHIPHILIC BLOCK COPOLYMERS VIA A COMBINATION OF RAFT POLYMERIZATION AND ROP

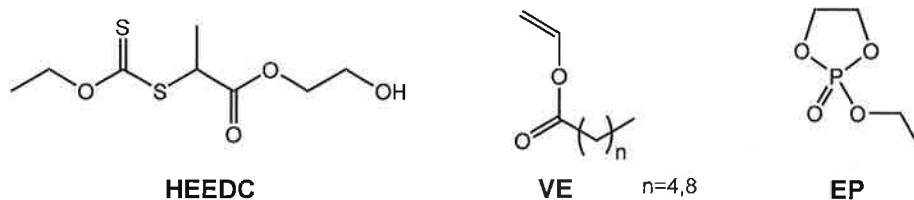
MARIA SCHACHNER <sup>a)</sup>, CLAUDIA DWORAK <sup>\*a)</sup>

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### Abstract

Micelles made from amphiphilic block copolymers received a steadily increasing interest over the past few years due to their versatile usage in the medical field (e.g. drug carrier systems). In this study we combined RAFT and ROP methods to obtain block copolymers made of fatty acid vinyl esters in the hydrophobic block and a cyclic phosphate monomer in the hydrophilic block. Such polymers are known to be biocompatible and biodegradable to FDA approved poly(vinylalcohol), fatty acids and phosphoesters as degradation products.

Controlled/living radical polymerization methods like Reversible Addition Fragmentation chain Transfer (RAFT) polymerization are in general very efficient tools for the preparation of polymers with defined molecular weights and narrow molecular weight distributions. Ring Opening Polymerization (ROP) is also a proper method for the synthesis of polymers with low polydispersity indices and controlled molecular weights.



**Figure 1:** Dual Initiator HEEDC and used monomers for the synthesis of the amphiphilic block copolymers

The dual initiator **HEEDC** which can be used either as RAFT agent or as initiator for ROP was successfully synthesized according to literature<sup>[1]</sup> by a two-step reaction. The cyclic phosphate monomer **EP** was also synthesized as described in literature<sup>[2]</sup>.

**HEEDC** was used to synthesize RAFT polymers with different molecular weights from fatty acid vinyl esters **VE** by using AIBN as thermal initiator and dry anisole as solvent. Furthermore, **HEEDC** served as initiator to perform ROP of **EP** at moderate temperatures. We were able to synthesize homopolymers with low polydispersity indices (<1.2) at good monomer conversions by means of RAFT polymerization and ROP, respectively.

In the next step, both types of macro initiators were used for the preparation of amphiphilic block copolymers. Here we varied the ratio of hydrophilic to hydrophobic block in order to find out which one is the best to generate micelles in aqueous media from those block copolymers.

The polydispersity indices of the generated polymers were determined by GPC. The monomer conversion for the RAFT polymerizations was calculated from <sup>1</sup>H-NMR spectra and thereof the molecular weight of the polymers. The number of repeating units of the ROP generated polymers were also derived from <sup>1</sup>H-NMR spectra, which allowed us to calculate their molecular weight. Finally, the amphiphilic behavior of these block copolymers in water was studied by DLS.

Summing up, we synthesized a dual initiator that was successfully used for RAFT polymerizations as well as for ROP. Furthermore, we were able to synthesize biocompatible vinyl ester and phosphate based block copolymers which show amphiphilic behavior in water.

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## TUNING $\beta$ -ALLYL SULFONES AS CHAIN TRANSFER AGENTS IN DIMETHACRYLIC PHOTOPOLYMERS

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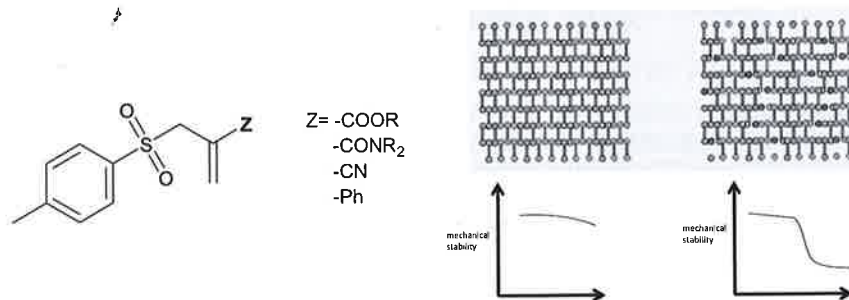


Figure 1:  $\beta$ -Allyl sulfones and the influence on the network architecture.

Addition fragmentation chain transfer agents (CTAs) are commonly used for controlling radical polymerization.<sup>1</sup> CTAs are usually known from thermal radical polymerization in solution, while photoinitiated bulk polymerization in the presence of CTAs is rarely described in literature. Generally, photopolymerization is recognised to be a fast, safe and environmentally friendly method for the synthesis of polymeric materials and has a broad area of applications.

By changing the uncontrolled radical chain reaction into a controlled radical chain growth/step growth process, lower molecular weights and narrow molecular weight distributions of the formed polymers can be achieved.<sup>2</sup> In this work, novel chain transfer reagents based on  $\beta$ -allyl sulfones were synthesized and investigated. The properties, molecular weights and the polydispersity of  $\beta$ -allyl sulfone modified methacrylate polymers are highly dependent on the electron withdrawing effect of the moiety, attached to the  $\beta$ -carbon of the  $\beta$ -allyl sulfone CTA. The photoreactivity, influence on the chain length, conversion of monomer and CTA, thermal and mechanical properties (photo-DSC, NMR, RT-NIR photorheology, DMTA,) of methacrylic resins and polymers with  $\beta$ -allyl sulfones as CTA, were investigated.

**Acknowledgement:** Financial support by IVAG and the Christian Doppler Society is kindly acknowledged.

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## STRUCTURE OF HYALURONAN IN ORGANIC SOLUTION

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### Introduction

Hyaluronic acid (also referred as HA or hyaluronan) is a linear polysaccharide made of repeating disaccharides of D-glucuronic acid and N-acetyl glucosamine linked by  $\beta(1\rightarrow4)$  and  $\beta(1\rightarrow3)$  glucosidic bonds (Figure 1). The molecular weight of this polymer in nature is very broad; it varies from several Kilo Dalton up to several Million Dalton.

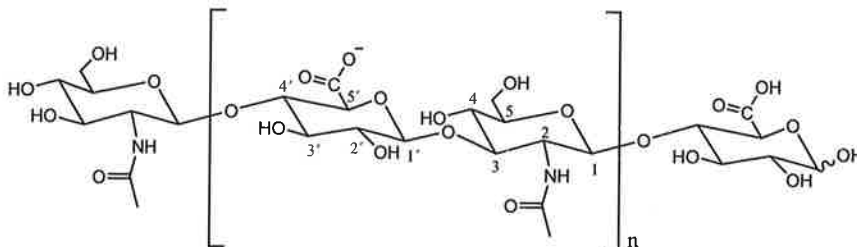


Figure 1: chemical structure of hyaluronan

To improve the chemical and physical properties in biological systems hyaluronic acid is chemically modified. Some modifications are performed in water, others need to be performed in organic solvents such as dimethylsulfoxide (DMSO) because of the use of water sensitive reagents [1]. For most derivatization reactions the transformation of hyaluronic acid to the acid form or to ammonium salt is required.

Over the past 50 years the structure of hyaluronic acid salts in aqueous solution has been intensively investigated [2], whereas conformation in organic solvent prior to chemical modification has been neglected, although this might have an influence on the distribution of the substituents along the polymer chain and consequently on the properties of the derivatives.

In this work we present the elucidation of the structure of hyaluronan in DMSO with and without the addition of salt for screening the interactions between polymer chains.

### Experimental

The solutions were analyzed by static and dynamic light scattering and small angle X-ray scattering. Intrinsic viscosity was determined by rheological measurements. Together, the Mark Houwink plot and the scattering methods indicate the conformation of hyaluronic acid in these systems.

### Results and Discussion

Hyaluronan in DMSO in salt free solution produces a high viscous solution characterized by big aggregates (hydrodynamic radius > 5000 nm). The addition of specific salts shields the ionic groups and prevent interactions with surrounding chains. These solutions are characterized by a low viscosity, easy filterability and low hydrodynamic radius. HA chains in this condition behave as thin rigid rods in solution.

**Acknowledgement:** The authors gratefully acknowledge the financial support from Croma Pharma (Austria).

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## MICRO STRUCTURAL PALS STUDY OF DIMETHACRYLATE NETWORKS

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Photopolymerization is an excellent technique for a wide variety of applications such as protective and decorative coatings or in the biomedical field. One major drawback is that common dimethacrylate photopolymerization usually creates uncontrolled, inhomogeneous, and rather brittle polymer networks.

Recently we were able to show that photopolymerization of dimethacrylates with  $\beta$ -allyl sulfones<sup>1</sup> as chain transfer agents leads to polymers with more controlled and homogeneous network architecture, similar to thiols, but without their well known drawbacks. These novel materials exhibit a sharpened gel point and are characterized by reduced shrinkage stress, increased conversion, and greater toughness in comparison to purely dimethacrylate-based polymers with broad thermal phase transition and brittle networks. The aim of this study is the characterization of the network structure on both the macro- and microscopic level. The method of choice here is positron annihilation lifetime spectroscopy (PALS) with the focus on estimating the size of free-volume holes ( $r_h$ ,  $V_h$ ) and the free-volume fraction  $f(T)$  of photo-cured materials through the mean ortho positronium (o-Ps) lifetime ( $\tau_3$ ).

Herein, we present the micro-structure study of a series of selected thermosets by using PALS. A mixture of urethane dimethacrylate and 1,10-decanediol dimethacrylate (2M) as reference and 2M with  $\beta$ -allyl sulfone (DAS) and tetra(ethylene glycol) dithiol (DT) as chain transfer agents were investigated. From the PALS measurement at RT we obtained the information that DAS containing sample with lower o-Ps formation has smaller voids than neat 2M but also DT-based sample. Also the shape of  $\tau_3$  distribution in DAS sample shows the presence of smaller voids with more uniform homogeneous microstructure in comparison with DT and 2M samples. These findings are in good correlation to the macroscopic characteristics of DAS sample, such as reduced shrinkage stress, sharpened glass transition and good impact resistance<sup>1</sup>. On the other hand,  $\tau_3$ -T dependence for DAS sample displays several different free-volume expansion regions that were characterized with regards to the size of free-volumes ( $V_h$ ) at glass transition temperature  $T_g$  as well as the expansion coefficients.

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## WATER SOLUBLE VISIBLE LIGHT PHOTOINITIATORS: Li-TPO AS HIGHLY REACTIVE AND SOLUBLE COMPOUND WITH EXTRAORDINARY STABILITY

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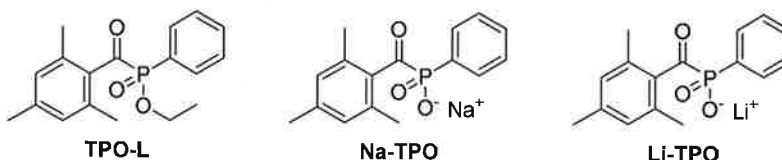
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### Abstract

Even though **Li-TPO** (lithium phenyl-2,4,6-trimethylbenzoylphosphinate) is known to literature for quite some years now it is not commercially available and was used only for very few special applications, for example synthesis of hydrogels for drug delivery systems.<sup>1</sup> This is remarkable since **Li-TPO** offers great advantages compared to other commercially available water soluble photoinitiator systems. It shows excellent solubility in high concentrations of approximately 100 g/L in water, has very high reactivity (70% monomer double bond conversion in aqueous systems under visible light irradiation), outstanding stability (no decomposition reactions in acidic or alcoholic environment at 42 °C over a period of 20 days), is biocompatible (tested in vitro with cell cultures) and last but not least is very easily accessible through a high yield (> 99%) synthesis with cheap starting materials. Another advantage is the ability to initiate under visible light (400-500 nm) irradiation, which even makes applications involving living cells possible.

**Na-TPO** (sodium phenyl-2,4,6-trimethylbenzoylphosphinate) and **TPO-L** (ethyl-(2,4,6-trimethylbenzoyl)-phenyl phosphinate) were used as reference compounds for our studies because of structural similarity and an identical initiation mechanism.



We tested **Li-TPO** in water based monomer formulations. In photo-DSC, storage stability, water solubility and biocompatibility measurements **Li-TPO** showed best results and it is furthermore a very promising compound for a whole variety of applications from 3D-printing of hydrogels to industrial color printing with water based ink formulations.

**Acknowledgement:** We thank the Christian Doppler Society for financial support.

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## SYNTHESIS AND CHARACTERIZATION OF MODIFIED STARCHES FOR PHARMACEUTICAL APPLICATIONS

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### Introduction

Starch is a biodegradable and renewable biopolymer that has been widely studied for many years in the food industry and also for non-food applications.<sup>1</sup> Modifications of starches are carried out to enhance the positive attributes and to eliminate the shortcomings of native starches. Various methods have been developed to produce a range of modified starches with a variety of characteristics and applications. Physically modified starches are simple and inexpensive because they can be produced without chemicals or even biological agents. Physical modifications are realized by heating up to temperatures above the gelatinization temperature to reorganize the spherical structure or by using an extrusion process. Chemical modifications are achieved by introducing suitable functional groups into starch molecules by using reactions like etherification, esterification, grafting or crosslinking. The last-mentioned is one of the most common ways to improve the properties of starch in a chemical way. Sodium trimetaphosphate (STMP), epichlorohydrin and phosphoryl chloride are some commonly used crosslinking agents. Among these compounds only STMP is FDA approved, non-toxic, and it is reported to be an efficient crosslinker for starch slurry at temperatures below and above the gelatinization temperature. Very recently, it has been found that starch phosphates are promising materials for the preparation of tablets for drug delivery due to high swelling and hydration capacity and improved disintegrating properties compared to unmodified starch.<sup>2,3</sup>

### Objective, Experimental and Results

In this study the suitability of several commercially available starch products (crosslinked, anionic, cationic, pregelatinized) and of starch phosphates with varying degree of phosphorylation as materials for tablets was evaluated. Starch was modified with STMP in a slurry process. The weight ratio of STMP to starch was varied and the reactions were performed at a constant temperature below the gelatinization point. In addition, starch was modified with STPM using an extrusion process. All starches were characterized by rheological measurements, FTIR spectroscopy and SEM. Water up-take was determined and additionally tablets of the commercial starches and freeze dried starch phosphates were prepared by a direct compression method. As expected, the highest water uptake was found for pregelatinized starch derivatives. Compared to native starch the water absorption of phosphorylated starches increased and the gelatinization temperature decreased, indicating the presence of monoesters and a rather low level of crosslinking. Also the extrusion process led to an improvement of properties relevant for materials for tablets.

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