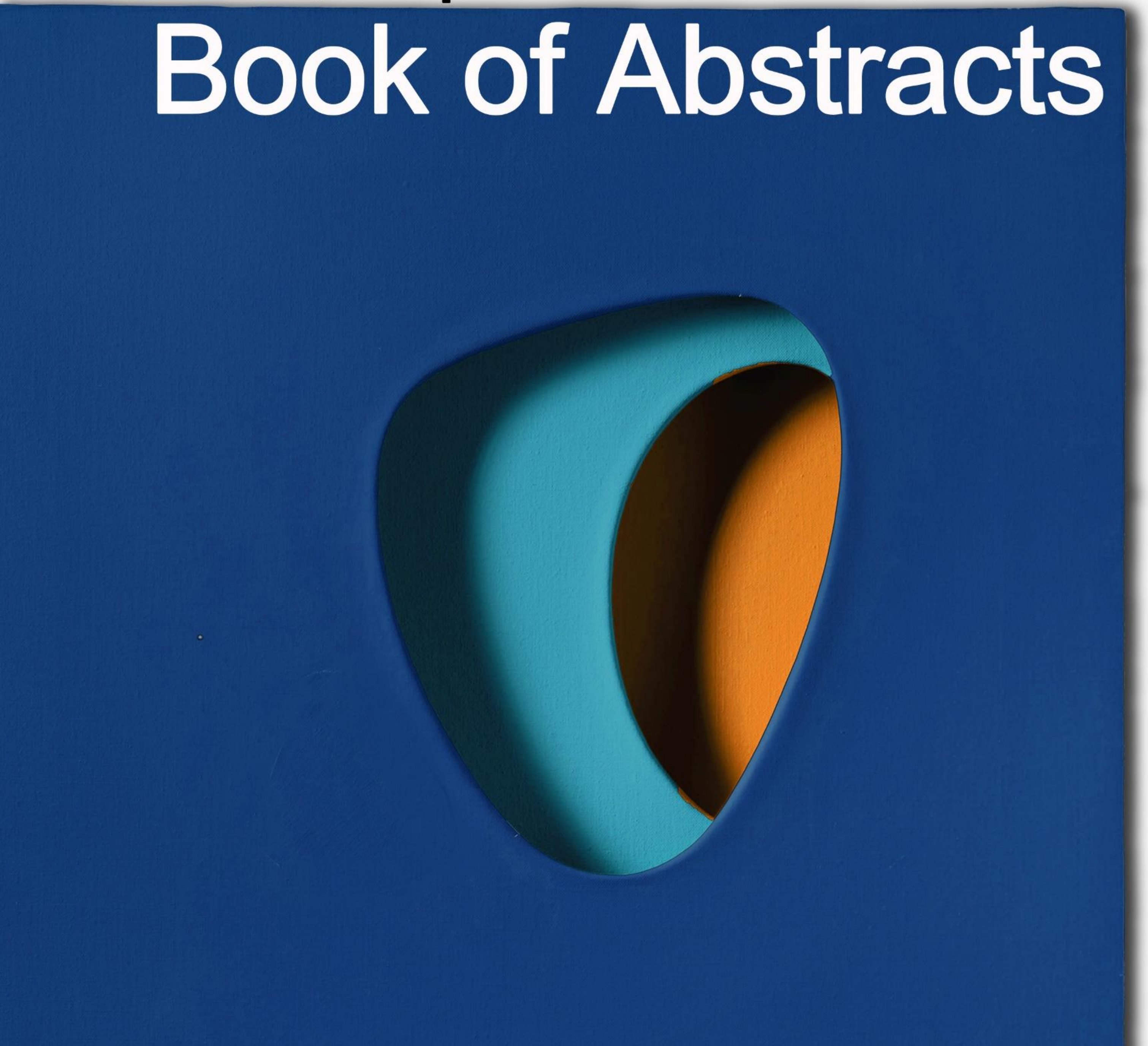
2024 YPRA

TU Graz
Graz University of Technology

Young Polymer Researchers Austria

Weiz, September 18-20, 2024

Book of Abstracts



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FOREWORD

Welcome to the first Young Polymer Researchers Austria (YPRA) meeting!

The YPRA is designed to bring together undergraduate and graduate students as well as early career postdoctoral researchers in the field of polymer science. The meeting provides a forum for the presentation of their research in the form of oral and poster presentations, and combines the science with ample time for networking and a panel discussion on the (probably) most pressing question for many of the participants: PhD is done, now what? Set in the beautiful surroundings of Weiz, the meeting will also include social activities such as summer curling and enjoying local specialities, allowing participants to meet future colleagues from polymer-related industries in the heart of Europe.
The first YPRA will be attended by around 60 participants, one sixth of whom will be from outside Austria, and will feature 28 oral and 17 poster presentations. The research topics cover a wide range, but are concentrated on two major topics, namely polymer photochemistry and covalent adaptable networks. In these two topics, the leadership of Austrian research groups is internationally recognised, as shown by the listing of two Austrian papers in the Polymer Chemistry's Most Popular 2023 Articles collection,[1] one article in the Polymer Chemistry and Catalysis Science & Technology cross-journal collection on 'Plastic Conversion'[2] and two papers in the Polymer Chemistry 15th Anniversary Collection.[3] It is therefore fitting that the two rising stars of Austrian polymer science who will give the invited Young Faculty Talks - Katharina Ehrmann and Elisabeth Rossegger - come from these research areas. The YPRA will also award a prize for the best oral presentation and a prize for the best poster to encourage the next generation of polymer scientists.
The YPRA meeting, if successful, will continue as a series of meetings to complement the Polymer Meetings, the biennial conference series organised by the polymer communities of Austria, the Czech Republic, Hungary, Slovakia and Slovenia. The next Polymer Meeting, number 16, will be held in Prague in September 1-4, 2025.
We all hope that you will find the YPRA enlightening, motivating and inspiring.

Sincerely,

Christian Slugovc,

on behalf of the organizing committee

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[1] a) Rossegger, E.; Shaukat, U.; Moazzen, K.; Fleisch, M.; Berer, M. Schlögl, S. *Polym. Chem.* **2023**, *14*, 2640. DOI: 10.1039/D3PY00333G; b) Kojic, D.; Ehrmann, K.; Wolff, R.; Mete, Y.; Koch, T.; Stampfl, J.; Baudis, S.; Liska, R. *Polym. Chem.* **2023**, *14*, 4809. DOI: 10.1039/D3PY00787A

[2] Ratzenböck, K.; Uher, J. M.; Fischer, S. M.; Edinger, D.; Schallert, V.; Žagar, E.; Pahovnik, D.; Slugovc, C. *Polym. Chem.* **2023**, *14*, 651. DOI: 10.1039/D2PY01345B

[3] a) Pieringer, F.; Knaipp, K.; Liska, R.; Moszner, N.; Catel, Y.; Gescheidt, G.; Knaack, P. *Polym. Chem.* **2024**, *15*, 2229. DOI: 10.1039/D4PY00445K; b) Bassenheim, D.; Mitterbauer, M.; Liska, R.; Knaack, P. *Polym. Chem.* **2024**, *15*, 2229. DOI: 10.1039/D4PY00343H

ACKNOWLEDGMENT

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Das Land
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is gratefully acknowledged.

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PCCL
Polymer Competence Center Leoben

CHASE

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and brought to stage by the work of the organizing committee consisting of Larissa Donner, Lena Hofbauer, Johanna Lang, Zuzana Reuter, David Schuster, Matthias Steiner, Peter Weiss, Gregor Trimmel and Christian Slugovc.

The organizers were supported by the advisory board of the YPRA consisting of Alexander Bismarck (Univ. Wien), Oliver Brüggemann (JKU), Wolfgang Kern (MUL), Robert Liska (TU Wien), Christian Paulik (JKU), Sandra Schlögl (PCCL), Christian Slugovc (TU Graz), Gregor Trimmel (TU Graz)

PROGRAM

Wednesday, Sept. 18, 2024

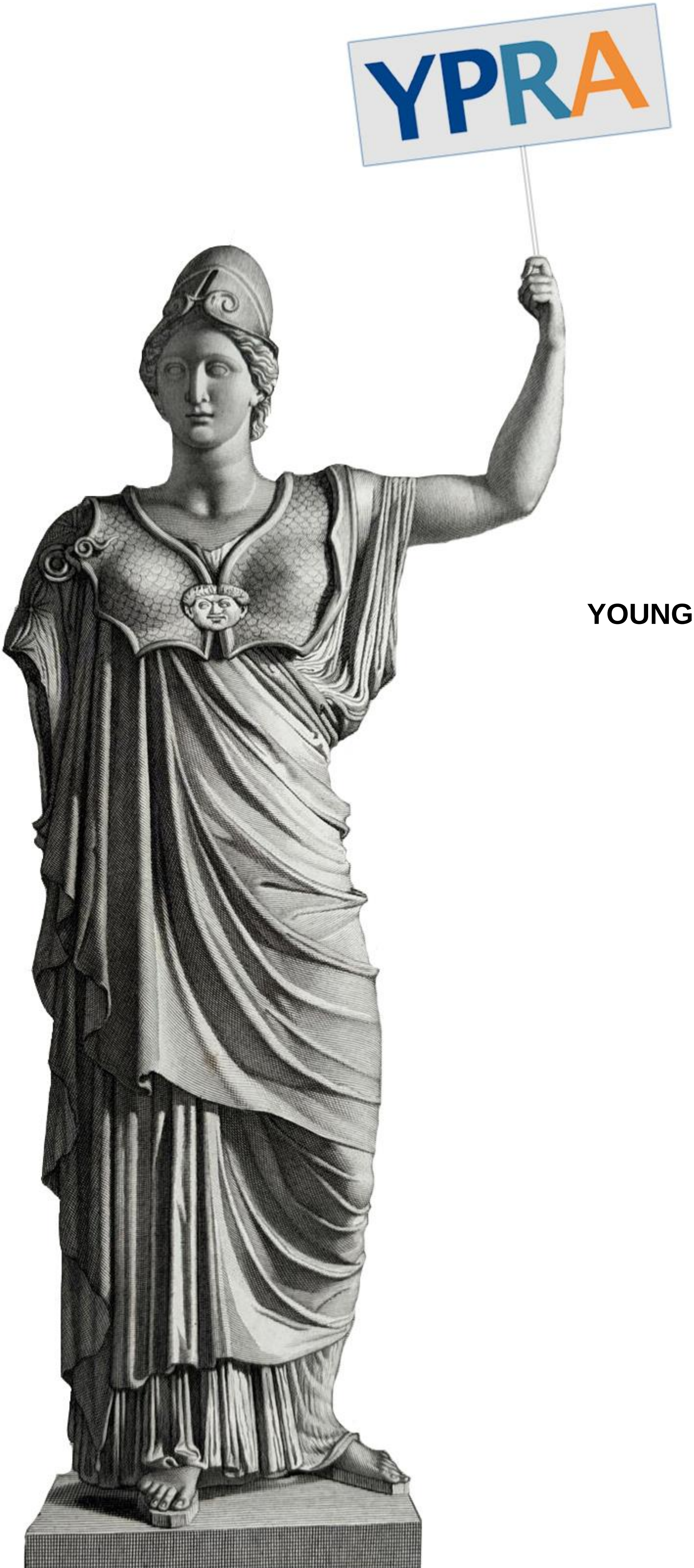
10:30-11:00	**Opening**
	Chairman: Christian Slugovc
11:00-11:20	**O1:** *Frontal polymerization of covalent adaptable networks.* Christoph Schmidleitner
11:20-11:40	**O2:** *3D Printing of polysaccharides imitating porcine aortae.* Florian Lackner
11:40-12:00	**O3:** *On the cleavage of alkoxyamines: Prospects of "smart" mediation systems for radical polymerization reactions.* Mathias Wiech
60 min	Lunch
	Chairwoman: Sandra Schlögl
13:00-13:40	**YFT1:** *Light ON – orthogonal photoreactions for adapting material properties.* Elisabeth Rossegger
13:40-14:00	**O4:** *Hydrophilic and semiconducting π-conjugated polyelectrolyte foams: Synthesis and photocatalytic activity.* Aleksander Saša Markovič
30 min	Coffee Break
	Chairman: Gregor Trimmel
14:30-14:50	**O5:** *Surface-shielded vectors based on cationic-hydrophilic di-block copolymers for improved gene delivery.* Eliška Hrdá
14:50-15:10	**O6:** *Antagonistic photoreactions – A key to controlled curing in thiol-ene networks.* Rita Johanna Höller
15:10-15:30	**O7:** *Synthesis and evaluation of novel MAPO-based photoinitiators.* Jelena Nikolic
15:30-15:50	**O8:** *An approach of characterization for inhomogeneous feedstock polymers: Rheometric investigations of post-consumer polypropylene recyclates.* Dominik Kaineder
30 min	Coffee Break
	Chairman: Christian Slugovc
16:20-16:40	**O9:** *In-situ release of carbenoid species from imidazoles and oxiranes for catalysis in polymer chemistry.* Matthias Steiner
16:40-17:00	**O10:** *Using light for preparation of synthetic polypeptides via ring opening polymerization of N carboxyanhydrides.* Petra Utroša
17:00-17:20	**O11:** *Advanced polymerization techniques in surface engineering.* Darshak Pathiwada
17:20-open end	**Poster Session** followed by **Grill Party** and **Summer Stockschießen** "Bloaflschmeißn"

Thursday, Sept. 19, 2024

	Chairman: Christian Slugovc
9:30- 9:50	**O12:** *Using polyolefin recyclates from end-of-life vehicles in automotive compounds.* Markus Gall
9:50- 10:10	**O13:** *Ring-opening copolymerization of epoxides and cyclic anhydrides in a novel photopolymerization approach.* Theresa Ammann
10:10- 10:30	**O14:** *Poly(2-isopropenyl-2-oxazoline) brushes as a platform for versatile surface functionalization.* Manisha Singh
30 min	Coffee Break
	Chairman: Gregor Trimmel
11:00- 11:20	**O15:** *Enzymes and polarity: a complex topic.* Lena Graf
11:20- 11:40	**O16:** *Acid-base properties of polyamidoamines derived from renewable Tulipalin A and diamine monomers.* Sambit Kumar Lenka
11:40- 12:00	**O17:** *High-performance photo base generators for visible light initiation of oxa-ene Michael addition reactions* Edma Gjata
60 min	Lunch
	Chairman: Robert Liska
13:00- 13:40	**YFT2:** 3D *printable crystalline photopolymer networks and their applications.* Katharina Ehrmann
13:40- 14:00	**O18:** *Evaluation of the efficiency of solvent-based recycling for high density polyethylene using Design-of-Experiment.* Dario Pindrić
30 min	Coffee Break
	Chairman: Robert Liska
14:30- 14:50	**O19:** *Novel polyurethane catalysts based on germanium(IV) compounds.* Christoph Garstenauer
14:50- 15:10	**O20:** *Development of smart polymers for battery safety applications based on a retro Diels-Alder reaction.* Daniel Bautista
15:10- 15:30	**O21:** *3D-Printed polysaccharide biomaterials: Comprehensive analysis of swelling, structural stabilization, and mechanical stability.* Miriam Zeller
15:30- 15:50	**O22:** *Innovative scalable synthesis of alternating acrylamide copolymers: Pathways to new applications.* Felix Leibetseder
30 min	Coffee Break
16:20- 17:20	**PhD is done, now what?** Panel discussion with Elisabeth Rossegger, Katharina Ehrmann, Nadja Noormofidi and Katharina Kodolitsch; moderation: Florian Lackner
19:00- open end	**Conference Dinner** at “Der Ederer”

Friday, Sept. 20, 2024

	Chairman: Christian Slugovc
9:30- 9:50	**O23:** *Covalently attachable photoacid generator in dynamic thiol-ene photopolymers for microscale manipulation of transesterification reactions.* Roman Korotkov
9:50- 10:10	**O24:** *Bio-responsive polymer probes/contrast agents for dual* $^{1}H/^{31}P$ *and* $^{31}P/^{19}F$ *magnetic resonance imaging.* Lucie Kracíková
10:10- 10:30	**O25:** *Copolymerization of epoxyeugenol and bisphenol A diglycidyl ether.* Johanna Lang
30 min	Coffee Break
	Chairwoman: Sandra Schlögl
11:00- 11:20	**O26:** *Alternative methods for covalent cross-linking of alginates.* David Bučak Gasser
11:20- 11:40	**O27:** *Bio-based photo-initiators for UV-Nano-imprint resins.* Philipp Melchior
11:40- 12:00	**O28:** *Design and characterization of poly(dicyclopentadiene) derived hard carbons as anode materials for sodium-ion batteries.* David Schuster
12:00- 12:15	**Award ceremony and Closing**
12:15	Lunch



YOUNG FACULTY TALKS

Light ON – orthogonal photoreactions for adapting material properties

Elisabeth Rossegger,* Walter Alabiso, Sandra Schlögl

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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 paves the way for the production of specific, adaptable and reliable polymers and can be used for the formation, degradation and functionalization of polymers. Material properties such as stiffness[1] and wettability[2] can be spatiotemporally adjusted, for example. Moreover, we have demonstrated in our recent work that it allows to locally introduce dynamic properties into photopolymer networks. Photolatent catalysts are a versatile concept for local control of 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 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) was exploited.[3,4] 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.[5,6] 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.

References:

1 Rossegger, E.; Strasser, J.; Höller, R.; Fleisch, M.; Berer, M.; Schlögl, S. *Macromol. Rapid Commun*. **2023**, *44*, 2370005. DOI: 10.1002/marc.202370005
2 Rossegger, E.; Hennen, D.; Griesser, T.; Roppolo, I.; Schlögl, S. *Polym. Chem*. **2019**,*10*, 1882. DOI: 10.1039/C9PY00123A
3 Rossegger, E.; Moazzen, K.; Fleisch, M.; Schlögl, S. *Polym. Chem*. **2021**, *12*, 3077. DOI: 10.1039/D1PY00427A
4 Rossegger, E.; Shaukat, U.; Moazzen, K.; Fleisch,M.; Berer, M.; Schlögl, S. *Polym. Chem*. **2023**, *14*, 2640. DOI: 10.1039/D3PY00333G
5 Alabiso, W.; Sölle, B.; Reisinger, D.; Guedes de la Cruz, G.; Schmallegger, M.; Griesser, T.; Rossegger, E.; Schlögl, S. *Angew. Chem. Int. Ed.* **2023**, *62*, e202311341. DOI: 10.1002/anie.202311341
6 Alabiso, W.; Li, Y.; Brancart, J.; Van Assche, G.; Rossegger, E.; Schlögl, S. *Polym. Chem*. **2024**, *15*, 321. DOI: 10.1039/D3PY01106B

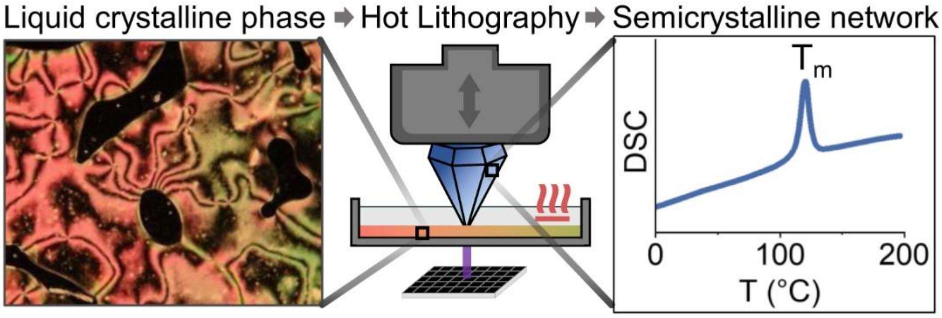
YFT2

3D printable crystalline photopolymer networks and their applications

Katharina Ehrmann,[a,*] Michael Göschl,[a] Dominik Laa,[b] Jürgen Stampfl,[b] Robert Liska [a]

[a] Polymer Chemistry and Technology Research Group, Institute of Applied and Synthetic Chemistry, Technische Universität Wien, Getreidemarkt 9/163, A 1060 Vienna, Austria; e-mail: katharina.ehrmann@tuwien.ac.at
[b] Institute of Materials Science and Technology, Technische Universität Wien, Getreidemarkt 9, 1060 Vienna, Austria

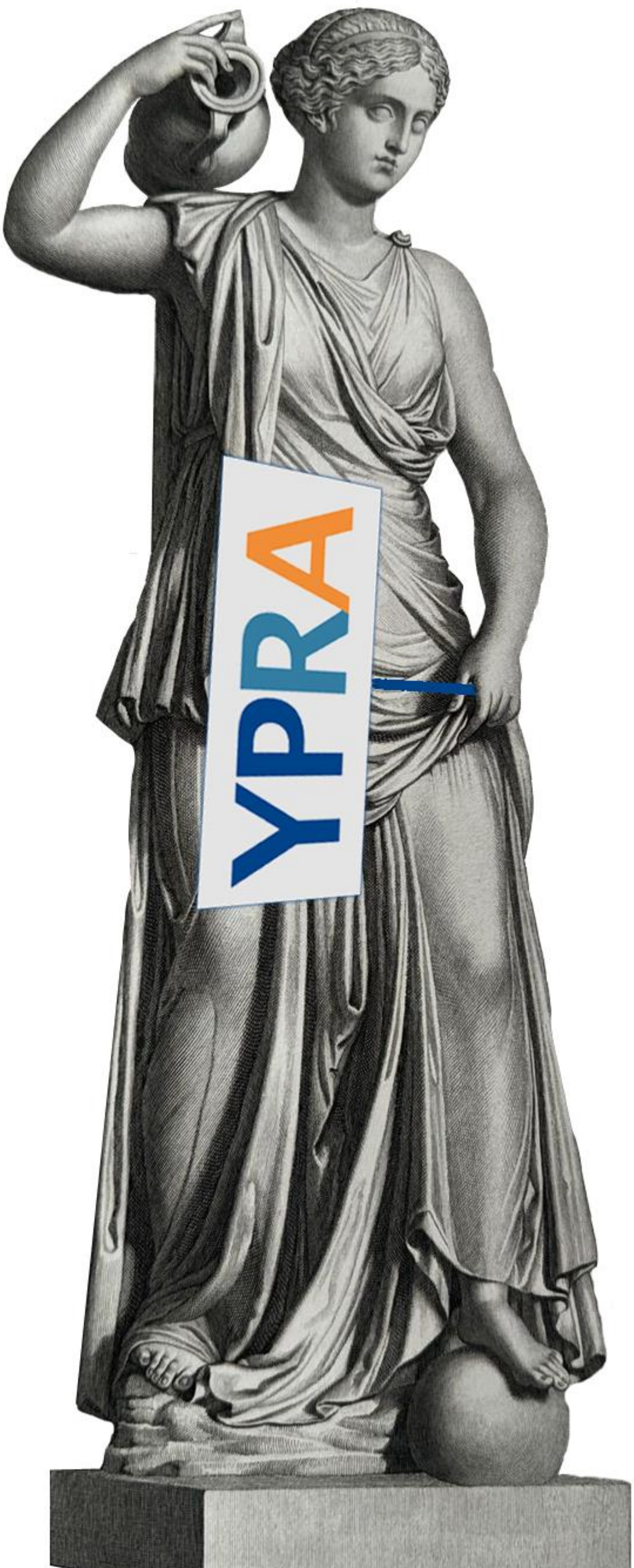
Conventional photopoylmernetworks typically exhibit amorphous morphology. In combination with their tendency for inhomogeneous and high crosslinking density, this renders the resulting materials brittle and unfunctional. Therefore, efforts to microstructure photopolymers have surged in the photopolymer community recently.[1] Herein, we present the synthesis and characterization of photopolymer networks from liquid crystalline thiol-ene formulations, effectively trapping their crystallinity in the main chain of the polymer network.



Concept of 3D printing crystalline photopolymer networks

We demonstrate lithographic 3D printing of crystalline objects with high fidelity via Hot Lithography. Their morphology enables efficient shapememory behaviour with very high rates of shape recovery and cyclability. By varying the printing temperature during the 3D printing process, we could further achieve multimaterial 3D printing of such crystalline domains in combination with elastomeric, amorphous domains. The achieved thermo-mechanical behaviour can therefore be varied from tough to elastomeric within one object, which promises interesting applications in combination with the highly efficient shapememory behaviour. Additionally, the difference between the optical properties of these two phases could be utilized in data storage applications.

References:
1. Ahmadi, M.; Ehrmann, K.; Koch, T.; Liska, R.; Stampfl, J. *Chem. Rev.* **2024**, *124*, 3978. DOI: 10.1021/acs.chemrev.3c00570



ORAL PRESENTATIONS

Frontal polymerization of covalent adaptable networks

Christoph Schmidleitner,[a] Matthias Kriehuber,[a] Sandra Schlögl,[a] Gregor Trimmel,[b]
Elisabeth Rossegger [a]

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[b] Graz University of Technology, Institute for Chemistry and Technology of Materials,
Graz, Austria

Frontal polymerization (FP) is defined as the conversion of monomers into polymers in a wave like manner (front).[1] The driving factor during this reaction is the heat generated by the exothermicity of the polymerization. Thus, only a local external energy input is required during the initiation process.[2] The used initial stimuli are usually either UV-light or thermal energy.

Consequently, shorter curing times can be achieved, larger objects can also be cured with light and less energy is required overall. Nowadays, beside energy efficiency also other material properties such as recyclability, reusability and reprocessability gain significance in polymer science. These can be implemented by introducing dynamic bonds into thermoset materials. Commonly, transesterification reactions between free hydroxy- and ester moieties are introduced by using suitable catalysts, such as organic phosphate esters, bases, Zn(II)-salts.[3]

In this work, we have combined the advantages of frontal polymerization and covalent adaptable networks. Radical frontal polymerization of thiol-acrylate resins (bearing ester and hydroxyl groups) lead to dynamic networks which undergo rapid stress relaxation at elevated temperatures and exhibit adjustable material properties depending on the amount of thiol used. This was confirmed by determining frontal properties as well as DMA measurements, demonstrating a decrease in reactivity and glass transition temperature with increasing amount of thiol. Additionally, photo-DSC measurements displayed a reduction in reaction enthalpy for higher amounts of thiol. Moreover, stress-relaxation tests at elevated temperatures were conducted to characterize the dynamic behaviour of the materials. The materials showed Arrhenius-dependent behaviour, which proves the existence of dynamic bond exchange reactions. To demonstrate the reusability of the investigated material, reprocessing tests were carried out which resulted in an 88.9 % restoration of the original Shore D hardness. The recovery of fillers such as glass fibers by decomposing the polymer matrix of a composite in ethylene glycol has also been verified.

References:

1 Suslick, B. A.; Hemmer, J.; Groce, B, R.; Stawiasz, K. J.; Geubelle, P. H.; Malucelli, G.; Mariani, A.; Moore, J. S.; Pojman, J. A.; Sottos, N. R. *Chem. Rev.* **2023**, *123*, 3237. DOI: 10.1021/acs.chemrev.2c00686
2 Malik, M. S.; Schlögl, S.; Wolfahrt, M.; Sangermano, M. *Polymers* **2020**, *12*, 2136. DOI: 10.3390/polym12092146
3 Rossegger, E.; Höller, R.; Reisinger, D.; Strasser, J.; Fleisch, M.; Griesser, T.; Schlögl, S. *Polym. Chem.* **2021**, *12*, 639. DOI: 10.1039/D0PY01520B

3D Printing of polysaccharides imitating porcine aortae

Florian Lackner,[a] Paola Šurina,[a] Julia Fink,[b] Petra Kotzbeck,[b] Jan Stana,[c]
Maximillian Grab,[d] Nikolaos Tsilimparis,[c] Tamilselvan Mohan,[a] Rupert Kargl,[a]
Karin Stana Kleinschek[a]

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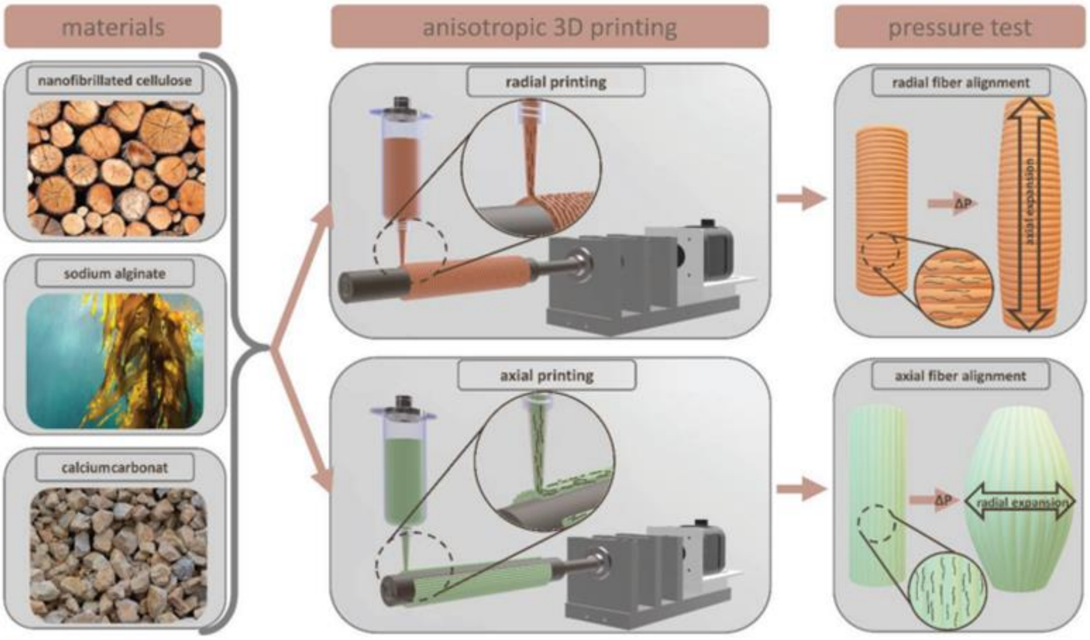
Nature exhibits an inherent capability to grow complex, anisotropic multilateral structures bottom up from simple molecules like glucose. This allows the construction of highly complex shapes with outstanding properties and functions.[1] In human aortae, circumferentially oriented collagen and elastin fiber networks enable unique strain stiffening anisotropic response in billions of repetitions.[2]



Overview of anisotropic 4-axis 3D printing process from Ref. 3

Herein we present the research results of our 3D printing experiments to create anisotropic structures from a nanofibrillated cellulose/alginate nanocomposite. The bioink received from mixing of the biopolymers and $CaCO_3$ nanoparticles could be processed with an extrusion-based 3D printer, allowing in-situ fiber alignment to produce scaffolds with anisotropic properties. The subsequent crosslinking with weak acids additionally enables the precise control of mechanical properties within one single printing process, to create sophisticated structures with tunable properties. Various tubes with different fiber alignment patterns could be 3D printed to demonstrate the anisotropic and water-resistant behavior of our material. Further the material was characterized to assess important biomedical parameters like cell compatibility, nutrient diffusion and controlled degradability.

References:

1 Gladman, A. S.; et al. *Nature Mat*. **2016**, *15*, 413. DOI: 10.1038/nmat4544
2 Tsamis, A.; et al. *J. R. Soc. Interface* **2013**, *10*, 20121004. DOI: 10.1098/rsif.2012.1004
3 Lackner, F.; et al. *Adv. Healthc. Mater.* **2024**, *13*, 2302348. DOI: 10.1002/adhm.202302348

On the cleavage of alkoxyamines: Prospects of “smart” mediation systems for radical polymerization reactions

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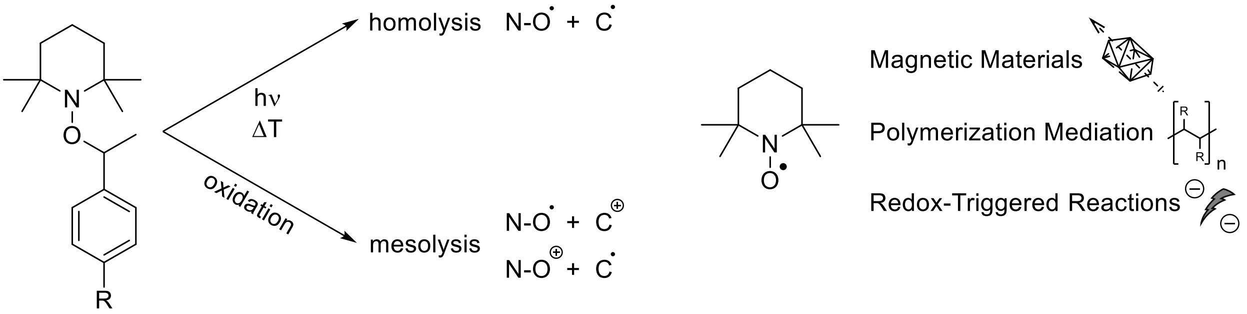
Alkoxyamines have attracted scientific interest due to their ability to decompose into radicals under mild and controllable conditions. Thermal and photochemical decomposition proceeds directly via C-O homolysis,[1] while oxidation of the parent alkoxyamine yields radicals by mesolysis of a radical cation intermediate.[2] The involved fragmentation pathways can however be complex and are highly dependent on the reaction conditions. Regardless of the exact mechanism, the decomposition 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.



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 illustrate how synergistically employing theoretical, electrochemical and spectroscopic (EPR/CIDNP) methods can shine light on the underlying fragmentation processes.

References:

1 Audran, G.; Blyth, M. T.; Coote, M. L.; Gescheidt, G.; Hardy, M.; Havot, J.; Holzritter, M.; Jacoutot, S.; Joly, J.; Marque, S. R. A.; Koumba, T. M. M.; Neshchadin, D.; Vaiedelich, E. *Org. Chem. Front.* **2021**, *8*, 6561. DOI: 10.1039/D1QO01276B

2 Hammill, C.L.; Noble, B. B.; Norcott, P. L.; Ciampi, S.; Coote, M. L. *J. Phys. Chem. C* **2019**, *123*, 5273. DOI: 10.1021/acs.jpcc.8b12545

O4

Hydrophilic and semiconducting π-conjugated polyelectrolyte foams: Synthesis and photocatalytic activity

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[c] Flemisch Institute for Technological Research (VITO), Boeretang 200, 2400 Mol, Belgium

Conjugated polymers (CPs) have a wide variety of applications, such as organic-light emitting diodes, organic field-effect transistors and organic photovoltaics, as well as for catalysis, energy harvesting and energy storage applications. A subgroup of these materials is known as conjugated porous polymers (CPPs), where if backbone pending or integrated ionic groups are added to CPPs these materials are known as conjugated porous electrolytes (CPEs). The addition of ionic groups gives these materials a specific set of properties combining semiconducting properties of CP with hydrophilicity. That's why, these materials are emerging as promising photocatalysts in aqueous environment, for cell imaging, water splitting, photodegradation or/and adsorption of pigments and small molecules, such as per- and polyfluoro alkyl substances or bisphenols that are an increasingly concerning problem for our society.[1] Therefore, we have developed a family of visible light active CPE foams by high internal phase emulsion (HIPE) templating, to perform degradation of a model compound bisphenol A (BPA), as a common additive used in plastics.

As part of the Upstream project (HORIZON-MISS-2022-OCEAN-01-04 Grant Agreement no. 101112877), three different CPE foams were developed using Sonogashira-Hagihara cross-coupling reaction as a polymerization chemistry and emulsion templating technique for structuring the porosity in the CPE network. Obtained CPE foams contain a semiconductive π-conjugated backbone with attached anionic, cationic and zwitterionic sidechains. These polymeric foams were then tested to remove BPA from water through adsorption and/or photooxidation. Direct Analysis in Real-Time coupled to Mass spectrometry (DART-MS) and Liquid Chromatography coupled to Quadrupole Time of Flight Mass Spectrometry (LC-QToFMS) were used and analyses showed that four main oxidation products are formed during photocatalysis and a 25 % reduction in BPA concentration compared to the initial solution. Since some of the observed oxidation products may form during the analysis itself (DART-MS analysis is performed (400 ºC)), LC-QToFMS was additionally performed to distinguish the products formed during the analysis from those formed during photocatalysis.

References:

1 a) Šorm, D.; Brus, J.; Pintar, A.; Sedláček, J.; Kovačič, S. *ACS Polym. Au* **2024**, in press. DOI: 10.1021/acspolymersau.4c00032; b) Jurjevec, S.; Žerjav, G.; Pintar, A.; Žagar, E.; Kovačič, S. *Catal. Today* **2021**, *361*, 146. DOI: 10.1016/j.cattod.2020.01.049 and references therein

Surface-shielded vectors based on cationic-hydrophilic di-block copolymers for improved gene delivery

Eliška Hrdá,* Ladislav Androvič, Michal Pechar, Richard Laga

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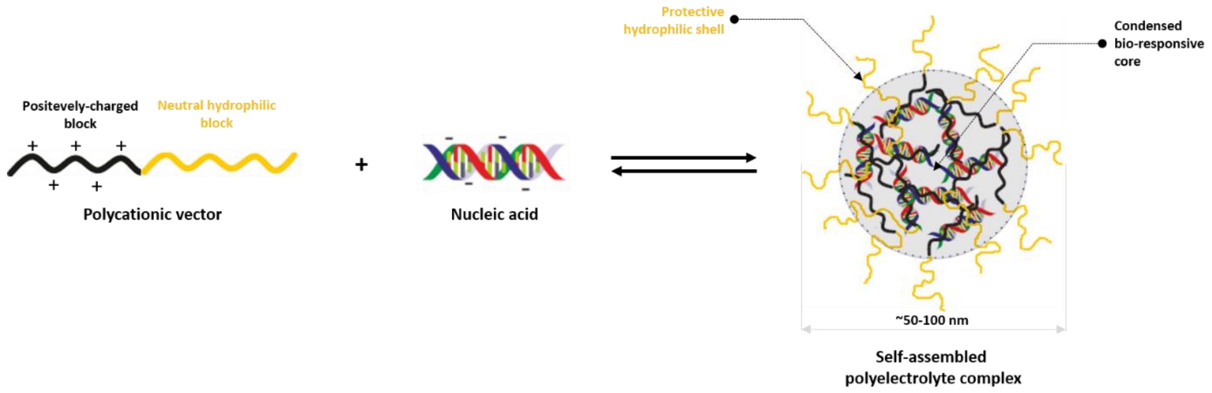
Gene therapy utilizing nucleic acid (NA) vectors represents a promising therapeutic strategy for treating various acquired and inherited diseases. However, developing a safe and efficient vector for systemic application remains a significant challenge. To address this, we have engineered a series of synthetic pH-sensitive polycationic vectors, based on methacrylate-type cationic-hydrophilic di-block copolymers. These vectors are designed to efficiently condense NAs into compact electrostatic complexes shielded by a layer of electroneutral hydrophilic polymer, which are stable in the bloodstream but disintegrate and release DNA inside the target cells.



A schematic illustration of the self-assembly/disassembly of the polycationic vector/NA complex.

The di-block copolymer vectors were synthesized by RAFT polymerization. The first (polycationic) block consisted of monomer units with permanently positively charged trimethylammonium or tributylphosphonium groups, linked to the polymer backbone via pH-sensitive hydrazone bonds, along with a minor fraction (0-20 mol%) of units with hydrophobic butyl groups. The second (hydrophilic) block was composed of an electroneutral polymer derived from either 2-methacryloyloxyethylphosphorylcholine or *N*-(2-hydroxypropyl)methacrylamide. The resulting vectors were well-defined ($Đ \leq 1.23$), with molecular weights of ~30–70 kg·mol^{-1}, forming 6–8 nm random coils in aqueous solutions. Electrophoresis and DLS experiments demonstrated that adding a molar excess of the polycationic vector to DNA ($P/N \geq 10$) formed electroneutral complexes with sizes ranging from ~140 to ~260 nm stable in physiological saline. The hydrolytic susceptibility of polycationic vectors was evidenced by the cleavage of their positively charged moieties in a mildly acidic environment, as determined through NMR spectroscopy. However, the anticipated disintegration of the complexes to liberate DNA was not observed under the model conditions. We contend, that this study establishes a robust foundation for further biological research and optimization for safe and effective gene delivery applications.

Acknowledgement: This research was financially supported by the Czech Science Foundation (Project No. 24-10980S).

Antagonistic photoreactions –
A key to controlled curing in thiol-ene networks

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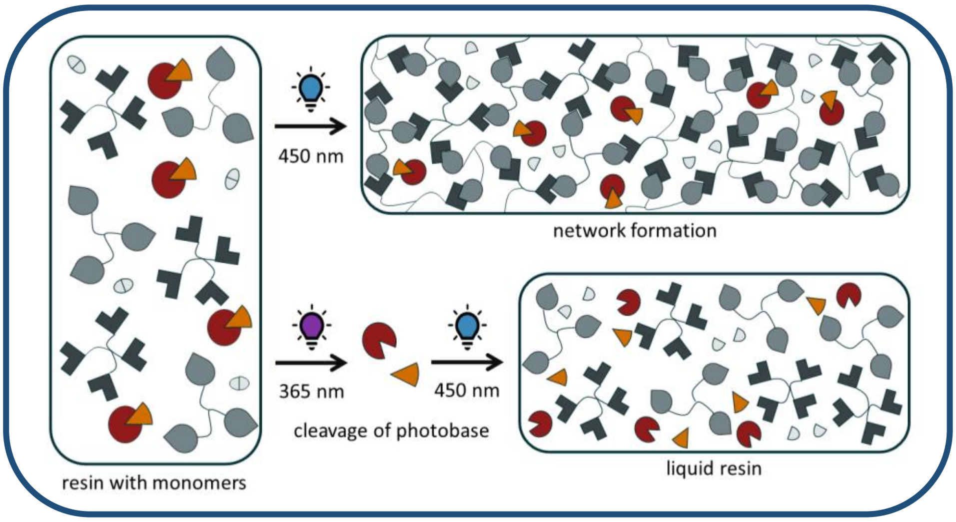
Thiol-ene chemistry has been a target of comprehensive research for several years, with a special focus on its use in photochemistry. Usually, thiol-ene free-radical reactions are a prominent example of click chemistry – showcasing high yields, a variety of possible monomers and orthogonality towards 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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Synthesis and evaluation of novel MAPO-based photoinitiators

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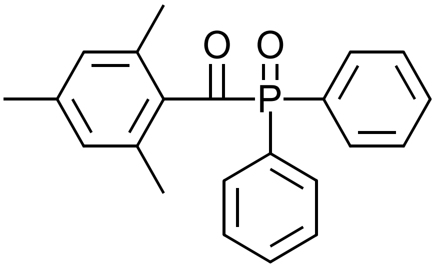
Most dental resins used for the restaurations are either photocurable or thermocurable.[1] Photocuring process offers several adventages including solvent-free working, high curing speed, better mechanical properties of the cured product and low energy costs.[2] In the photopolymerizable formulations, photoinitiators play a crucial role because they directly influence the final properties of the polymerized product. The requirements for such photoinitiator are therefore high reactivity, good compatibility, and solubility in formulations, as well as low toxicity, and no yellowing.[3]

Acylphosphine oxides (MAPOs) represent promising Type I photoinitiators since they meet most of the mentioned requirements.



Commercially available MAPO

This work focuses on the development of novel MAPO photoinitiators with a higher reactivity and bathochromic shift when compared to existing state-of-the-art MAPO molecules. Given the ability of heteroatoms on phosphorus to impact the efficiency of photolysis and absorption range, our focus is on exploring the effects of various substituents with different electronic influences. In this work, we focused primarily on synthesis of derivatives containing new phosphorus-heteroatom bonds, where the heteroatoms show either higher or comparable electronegativity to carbon atom, that is present in commercially available MAPO molecules. The goal is thereby to understand how these substituents influence the absorption and overall performance of the newly synthesized photoinitiators when compared to the established MAPO photoinitiators.

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An approach of characterization for inhomogeneous feedstock polymers: Rheometric investigations of post-consumer polypropylene recyclates

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Polymer processing of performance-oriented plastics led to their use in nearly every sector of the global market. Therefore, even single use packaging products implicate extensive research and development. Today, there are numerous virgin material grade polyolefines, which are modified to each application. However, to reduce the irrecoverable consumption of natural resources like oil and gas, recycling materials of vastly used packaging plastics like polyethylene (PE) and polypropylene (PP) must be used. Here, the specification of recycled polyolefin granules is rather scarce, often including a wide-ranging Melt Flow Rate (MFR) as sole classification parameter for processing application. Rheometric tests with an oscillating parallel plate provide a more accurate and sophisticated characterisation method.[1] Nevertheless, the classification of incoming recycled post-consumer raw materials remains a challenge, since recycled granules may fluctuate extensively in terms of material homogeneity as well as flow properties.

Therefore, the aim of this work was to develop a novel approach of industrial rheometric testing of post-consumer PP recyclates concerning their homogeneity and viscosity. For that purpose, a parallel plate rheometer and a single screw extruder with a rheometric die were used to define the viscosity of different recycled feedstock PP, while virgin grades were used as control material. Both sets of results were compared to the specified MFR. Findings of this work include a precise correlation between extrusion as well as oscillatory rheometry.[2] Systematic quantifiable fluctuations between batches were found in contrast to deviating results of MFR spot checks. Lastly, a novel calculation approach for viscosity of post-consumer PP, containing granules of different viscosities, was created, which takes the molecular degradation of an extrusion process into account.

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O9

In-situ release of carbenoid species from imidazoles and oxiranes for catalysis in polymer chemistry

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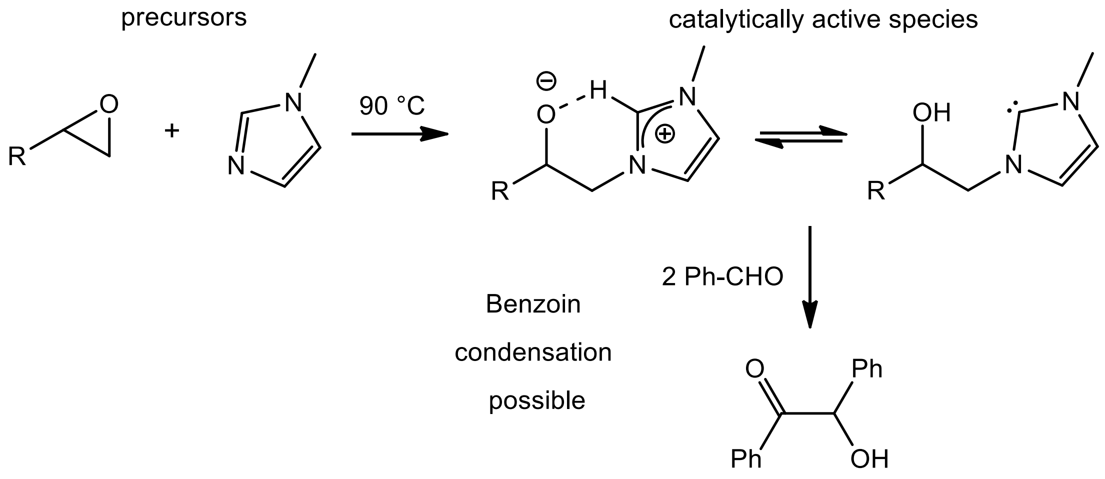
Organocatalysis has emerged as a valuable tool for sustainable polymer synthesis.[1,2] In this context, carbenes have received particular attention due to their high nucleophilicity, which enables reactions not possible with many other catalysts. A major drawback of carbenes is their sensitivity to moisture and oxygen, which prevents their use in many applications. Recent approaches use thermally triggered in situ carbene release to mitigate this problem.[3]



Oxiranes and imidazoles react at elevated temperatures to release carbenoid species being able to promote the benzoin condensation

Here we present our contribution to thermally triggered carbene release via a strategy involving imidazole and epoxy derivatives. Mechanistically, the attack of the imidazole on the oxirane ring releases a zwitterion consisting of an alkoxide and an imidazolium ion, which is plausibly in equilibrium with its charge-neutral carbene formed upon intramolecular deprotonation of the imidazolium. The carbenoid nature of these species was demonstrated by performing the benzoin condensation, a reaction that can only be catalyzed by cyanide ions and carbenes, using different epoxides and 1-alkylimidazoles as precursors. The reactivity of this cheap dual catalytic system can be exploited in various polymerization reactions but also in the chemical recycling of polymers, as demonstrated by the glycolysis of poly(ethyleneterephthalate) bottles.

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O10

Using light for preparation of synthetic polypeptides via ring-opening polymerization of *N*-carboxyanhydrides

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Light is an attractive trigger for polymerization as it can be controlled both temporally and spatially. Consequently, photoinduced polymerizations have become important for the additive manufacturing of polymers. Ring-opening polymerization (ROP) of *N*-carboxyanhydrides (NCAs) provides a modular platform for the preparation of synthetic polypeptides that have great potential for biomedical applications. Light can be used in two ways for the preparation of synthetic polypeptide materials. In the first approach, we prepare a polypeptide macromer by ROP of NCA and post-polymerization modification with photoresponsive groups that allow subsequent photocrosslinking (Figure 1A).[1] Alternatively, photocaged amines open up possibilities for photoinduced ROP of NCAs (Figure 1B). We focused on inducing ROP by using 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 NCAs.

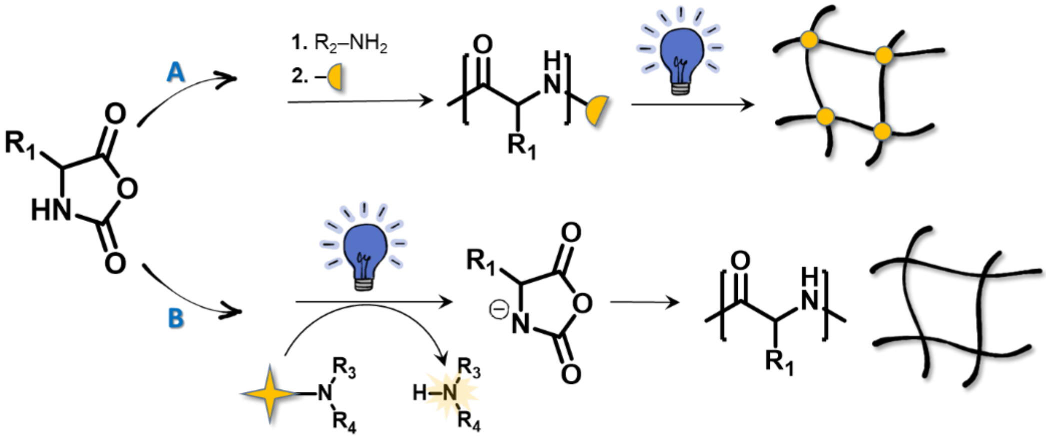

Figure 1. Using light for preparation of synthetic polypeptides. (A) Photocrosslinking of chain end functionalized synthetic polypeptide prepared by ROP. (B) Photoinitiated ROP of NCA using a photocaged amine.

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O11

Using polyolefin recyclates from end-of-life vehicles in automotive compounds

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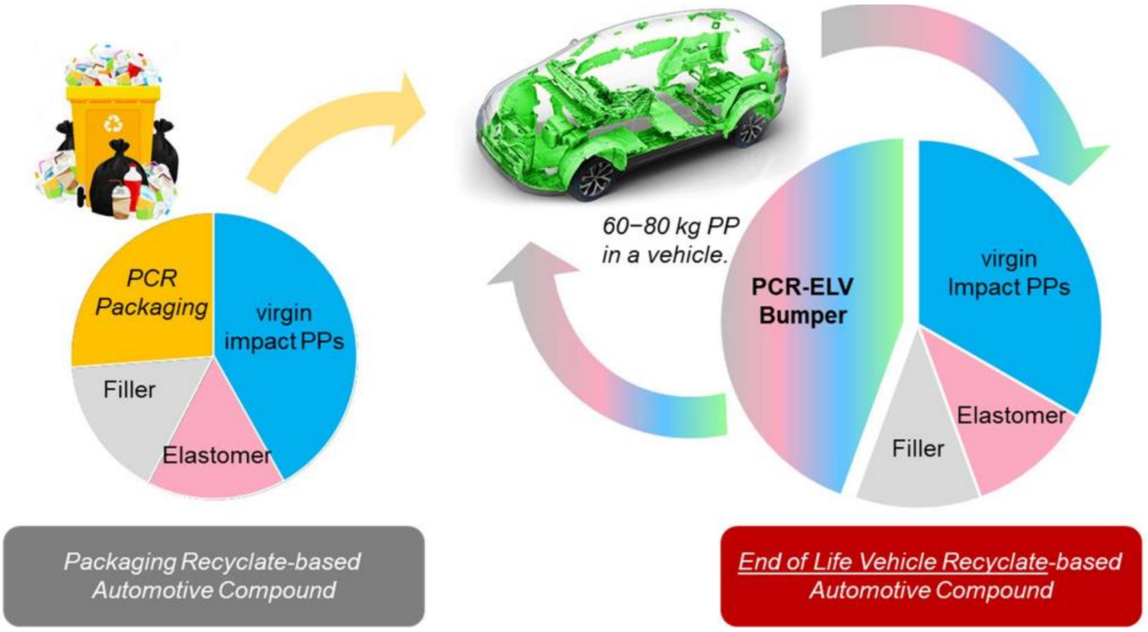
Increasing recycled plastics content in cars to 25% by 2030 is one of the key measures for decarbonising the automotive industry defined by the European Commission.[1,2] This should include end-of-life vehicle (ELV) recovery,[1,2] but such materials are presently hardly used in compounds.[3] To close the knowledge gap, two ELV recyclate grades were analyzed in comparison to a packaging-based post-consumer recyclate (PCR). The composition data were used to design polypropylene (PP) compounds for automotive applications with virgin base material and mineral reinforcement, which were characterized in relation to a commercial virgin-based compound. A compound with 40 wt.-% of ELV-based bumper recyclate can even exceed one with just 25 wt.-% of packaging-based recyclate in terms of stiffness/impact balance. While the virgin reference can nearly be matched regarding mechanics, the targeted flowability level is not reached by any of the PCR compounds, making further development work necessary.



Idealized increase of recycled content in automotive compounds by using ELV recyclate.

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Advanced polymerization techniques in surface engineering

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The development of polymerization techniques, such as atom transfer radical polymerization (ATRP), has enabled the creation of densely packed polymer brushes. By leveraging ATRP's attributes in combination with various functional monomers, desired properties such as hydrophobic or hydrophilic characteristics, bio-resistance or bioactivity, low-friction attributes, and anti-corrosiveness etc., can be achieved.[1] Photoinduced atom transfer radical polymerization (Photo-ATRP) stands out among ATRP methods due to its cost-effectiveness, improved oxygen tolerance, milder reaction conditions, and the ability to achieve temporal control without additional chemicals.[2,3] These features make Photo-ATRP in surface modification via SI-PhotoATRP a valuable tool for synthesizing well-controlled polymer brushes over large areas with minimal reaction volumes.[4]

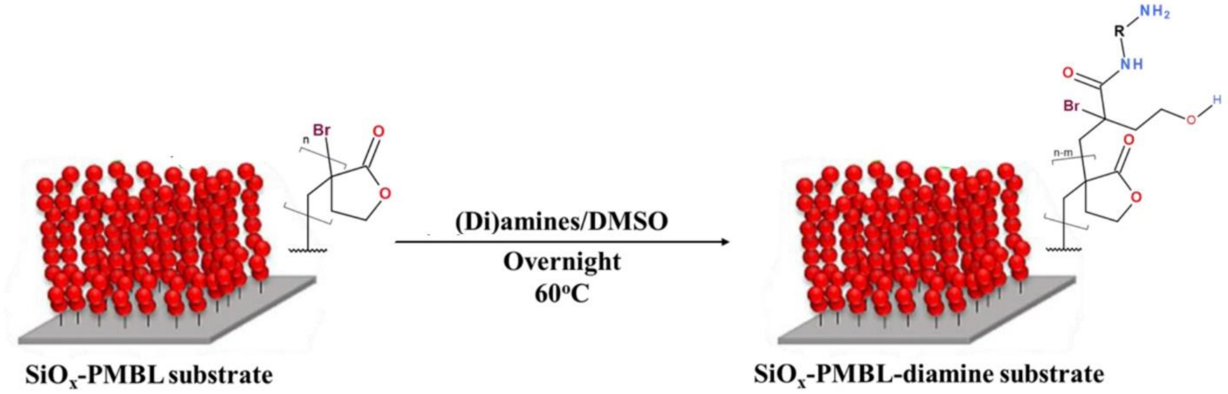

Figure 1. Post-polymer functionalisation of PMBL brushes using diamines.

Our study demonstrates the synthesis of highly dense and uniform PMBL (poly α-methylene-γ-butyrolactone) 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. Keeping in line with global emphasis on sustainable practices, our studies were optimised to reduce, reuse wherever possible. Encouraged by our findings, we extended the process to include modification of other surface oxide layers such as Al_2O_3, HfO_2, ZnO and TiO_2. Additionally, by taking advantage of multi-functionality of monomer such as MBL, we performed various post-polymer modifications to introduce anti-bacterial properties, biomolecular conjugates, and even antibodies for detection of cancer cells.

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Ring-opening copolymerization of epoxides and cyclic anhydrides in a novel photopolymerization approach

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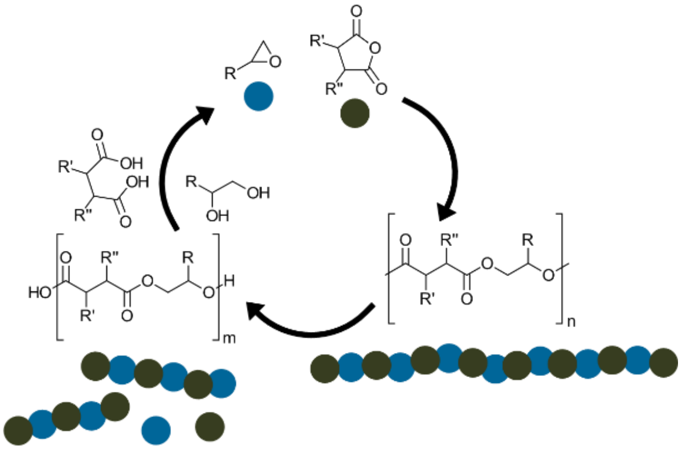
In recent years, degradability and recyclability of thermosets has been increasingly researched to reduce plastic waste in the environment and offer chances for recycling processes. In this regard, pure polyester networks offer an ideal opportunity since they contain hydrolysable ester bonds and usually afford benign degradation products.[1] Furthermore, using 3D printing allows for ecologically and economically favorable production of complex customized parts.



Proposed recycling mechanism of polyesters produced by ring-opening copolymerization of epoxides and anhydrides.

A relatively novel synthesis method for producing polyesters is the ring-opening copolymerization (ROCOP) of epoxides and anhydrides that combines many advantages associated with either the traditional condensation reaction or ring-opening polymerization. Previous reports regarding this reaction type have focused on organometallic catalysts, organic bases and Lewis base/Lewis acid pairs.[2] However, no attempts of using photocatalysts for ROCOP have been reported to date. Therefore, we have identified photoacid generators (PAGs) and photobase generators (PBGs) as possible catalysts for this ROCOP reaction, which would enable light-based 3D printing of the polyester materials. We have confirmed experimentally that both PAGs and PBGs are able to initiate ROCOP. However, significant amounts of side products, e.g. from homopolymerization of the epoxide, make PAGs unsuitable for producing pure polyester networks. Therefore, we have optimized linear photopolymer systems using PBGs as catalyst. The influence of temperature, light intensity, PBG concentration, and monomer and PBG structures regarding the stability of the formulations and the properties of the produced polyesters have been investigated. Subsequently, polymer networks using multifunctional epoxides were produced and investigated. Preliminary degradation studies demonstrate the successful full degradation of these polymer networks.

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Poly(2-isopropenyl-2-oxazoline) brushes as a platform for versatile surface functionalization

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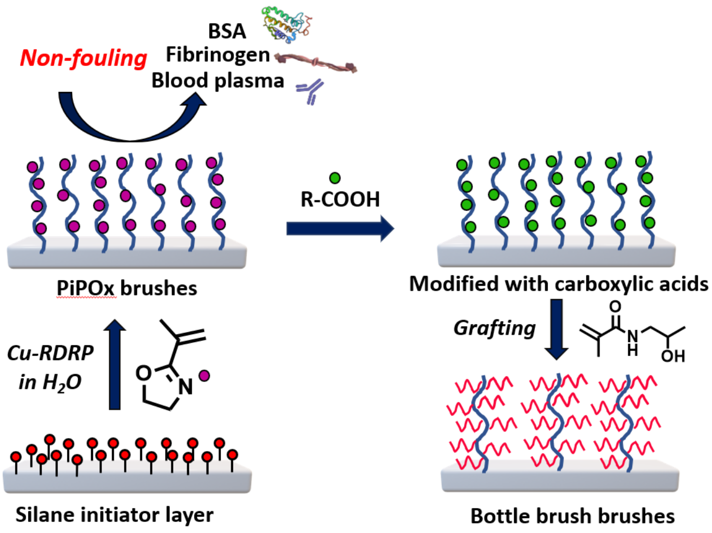
2-Isopropenyl-2-oxazoline (IPOx) is a significant double functional monomer with numerous applications.[1] However, until now there are no conditions which allow for precise control of surface-initiated PIPOx brush growth under the conventional Copper mediated reversible-deactivation radical polymerization (Cu-RDRP) conditions. In this study, we demonstrate that IPOx can be polymerized through Cu-RDRP with unprecedented control using 11-(trichlorosilyl)undecyl-2-chloropropanoate initiator and $CuCl/CuCl_2$ with HMTETA or $Me_4CYCLAM$ catalytic system in an aqueous medium from silicon surface. The potential of PIPOx brushes is then exemplified by incorporating different functionalities on the surface via modification of pendant 2-oxazoline rings using different carboxylic acids[2] under optimized reaction conditions.

Hydrolysis of the oxazoline rings with hydrochloric acid is also achieved in this work. Importantly, functionalization with azide-bearing carboxylic acids enabled the brushes to participate in copper-catalyzed alkyne–azide cycloaddition reaction (CuAAC). In addition, we also show that the prepared PIPOx brushes can be transformed into well-defined ATRP macroinitiators for subsequent grafting of a different polymer thereby yielding "bottle-brush" brushes with precisely controlled structure. Taken together, the optimized PIPOx brush polymerization and modification procedures provide a robust and versatile avenue for imparting functionality on a surface.



Surface functionalization by PIPOx followed by post-polymerization modification

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Enzymes and polarity: a complex topic

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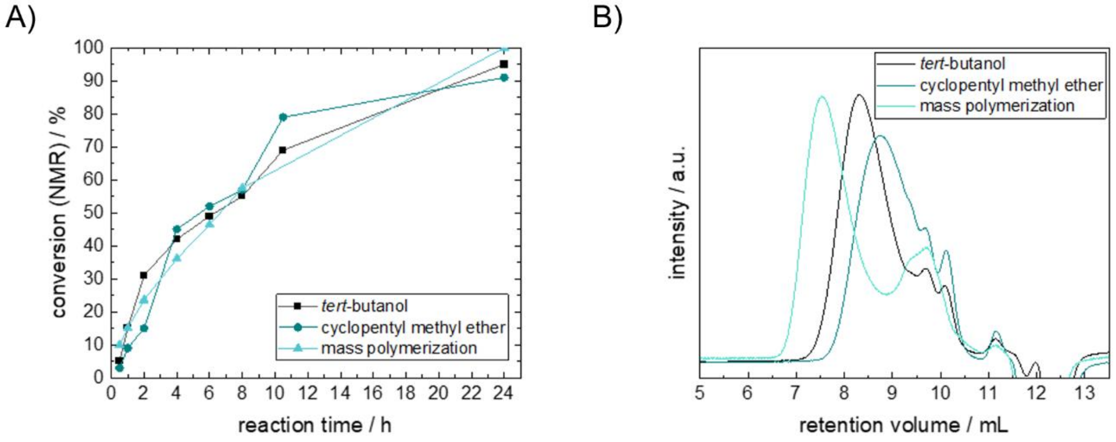
Polyesters are multi-facetted polymers, finding applicability in fields such as coatings, textiles and biomedical applications. Regarding conventional polyester synthesis, monomers are heated to temperatures of up to 240 °C and the reaction is performed in melt by commonly using metal-based catalysts. Another approach regarding polyester synthesis is the usage of enzymes, which includes benefits such as lower reaction temperatures, high selectivity and being nontoxic.

When using enzymes in polyester synthesis, mass polymerizations or polymerizations in solvents are two reaction systems commonly employed. Regarding mass polymerizations, at least one type of monomer must be liquid at the targeted reaction temperature. Mass polymerizations have numerous advantages, such as the lack of solvent which has to be removed after the reaction. Still, especially when regarding biobased monomers the melting points of the monomers are often not sufficiently low. Therefore, solvents must be introduced to achieve a homogeneous reaction mixture. While the concepts of both approaches appear to be straightforward, the identification of suitable reaction conditions is rather complex. This stems from the enzmatic catalyst's sensitivity towards factors such as reaction temperature and polarity of solvent and substrates. The extent to which each of these factors affects the enzymes' activity is interdependent.

Our group has developed a novel reaction system which aims to combine the benefits of both approaches while circumventing their disadvantages. We focus on the selection of biobased monomers and solvents, whereas one further prerequisite regarding the latter is having low boiling points. The monomers are enzymatically oligomerized in a solvent-aided homogeneous mixture. After sufficient esterification, the solvent is then removed by applying vacuum and the reaction is subsequently continued in mass. The aim of this investigation is to fascilitate a better understanding of the aforementioned interdependence of temperature and polarity in terms of enzyme activity.



A) Conversion of enzyme-catalyzed polyester synthesis reactions in two different bio-based solvents, whereas the solvent is removed after 8 h in comparison to a mass polymerization during 24 h reaction time and B) size exclusion chromatograms of each reaction after 24 h reaction time.

Acid-base properties of polyamidoamines derived from renewable Tulipalin A and diamine monomers

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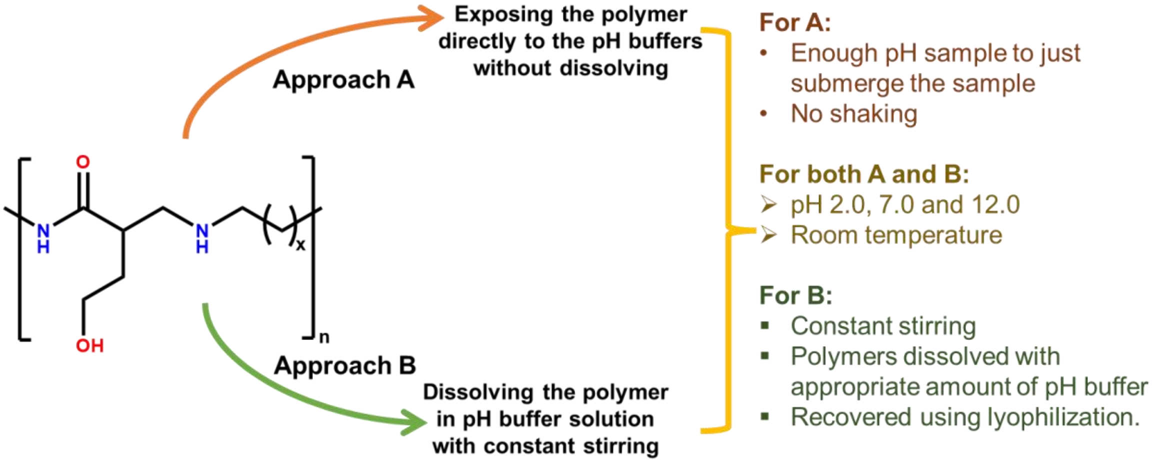
Step-growth polymerisation is advancing significantly, enabling the direct incorporation of functional groups into polymer backbones due to methods like Click chemistry, Michael addition, and Diels-Alder reactions.[1] Renewable monomers sourced from plants or bio-feedstocks provide a sustainable alternative to petroleum-derived materials due to their environmental benefits, potent biocompatibility, and reduced toxicity. Examples include itaconic acid, amino acids, and diamines.[2] Tulipalin A (α-methylene-γ-butyrolactone or MBL), a renewable monomer obtained from tulip flowers and derived from itaconic acid, can be utilised in various polymerisation techniques to create functional polymers.[3] Diamines sourced from bio-feedstocks or synthesised enzymatically participate in Michael addition with acrylates. While itaconic acid has been well-studied in this context, MBL's potential for Michael addition in polymer synthesis remains underexplored.



For A:
- Enough pH sample to just submerge the sample
- No shaking

For both A and B:
- ➢ pH 2.0, 7.0 and 12.0
- ➢ Room temperature

For B:
- ▪ Constant stirring
- ▪ Polymers dissolved with appropriate amount of pH buffer
- ▪ Recovered using lyophilization.

Figure 1. Schematic representation of pH degradation of synthesised polyamidoamines.

This study investigates a polyaddition step-growth polymerisation method using MBL and diamines to synthesise poly(amidoamine)s (PAAs) without solvents, followed by post-polymerisation modifications. The resulting PAAs, which feature unique functional groups both within the main chain and at the chain ends. Furthermore, this study examines the degradation of the polymer under various pH conditions (figure 1) to potentially recover and reuse fragments, thereby assessing the recyclability of these bio-based polymers.

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High-performance photo base generators for visible light initiation of oxa-ene Michael addition reactions

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In the ever-growing realm of new photoinitiators that shift the attention towards photogeneration of an acid or a base, photobase generators (PBGs) have gathered momentum in the last decade. They are superior to their radical generating counterparts, as they do not suffer from oxygen inhibition and are usually linked to a significantly lower volume shrinkage of the final material upon illumination.[1] Moreover, unlike acid initiating species, they do not corrode metallic substrates, rendering their application in coatings for automotive and electronic industries possible.[2]

However, most literature-known PBGs suffer from a rather weak basiticy of the active species (e.g. primary or secondary amines), short wavelength absorption confined within harmful UV light, low quantuum yields, as well as poor thermal and chemical stabilities.[1,3]

The work presented herein opts to overcome the aforementioned challenges through synthesis and investigation of new PBGs. Paired with their ability to liberate extremely strong phosphazene superbases with an impressive efficiency, their photosensitive moieties are designed to allow absorption of the incident light at high wavelengths, even extending to the visible light region. Characterization of their thermal behavior and photoreactivity was carried out via thermogravimetric analysis and UV/Vis spectroscopy.

The applicability of the prepared PBGs was tested on an oxa-Michael addition model sytem in a photo-DSC setup. Firstly, a monofunctional study was carried out including thorough screening of reaction conditions. This approach was further extended to a difunctional system, with successful attempts towards expanding the library of photopolymerization reactions that involve an oxa-Michael addition mechanism.

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Evaluation of the efficiency of solvent-based recycling for high density – polyethylene using Design-of-Experiment

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The global production of post-consumer recycled plastics reached 35.5 million tons in 2022, only counting mechanical and chemical recycling.[1] With the usage of solvent-based recycling, this number can be increased significantly.

This work focuses on the Design-of-Experiment (DoE) analysis of challenge-tests to determine the effectiveness of the solvent-based recyling process using the dissolution-precipitation method.[2-3]

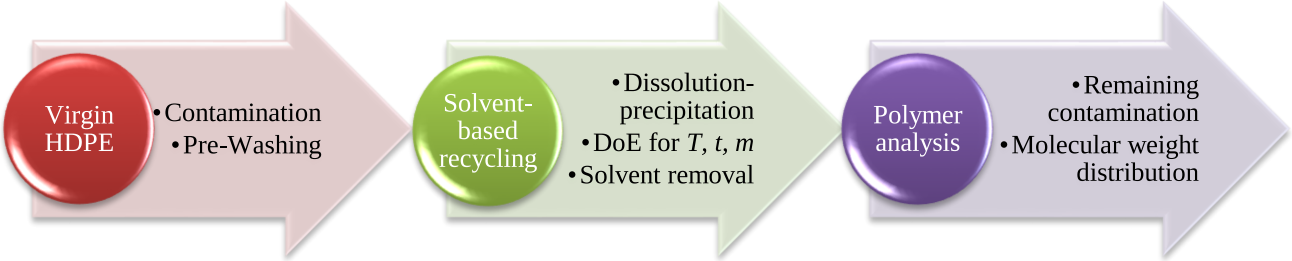

Figure 1: Process scheme for the challenge-tests.

For the DoE, a response surface model called Box-Behnken design is used, limiting the tested variables to three. To evaluate the dissolution process, the dissolution temperature (T), the dissolution time (t), and the amount of solvent (m) are chosen as parameters. These factors are correlated to the remaining contamination in the polymer and the molecular weight distribution (MWD). Therefore, virgin HDPE flakes are contaminated with a known concentration of nine different surrogates, which are analyzed using Gas Chromatography with Flame Ionization Detection (GC-FID). The MWD is determined with High Temperature - Size Exclusion Chormatography (HT-SEC).

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O19

Novel polyurethane catalysts based on germanium(IV) compounds

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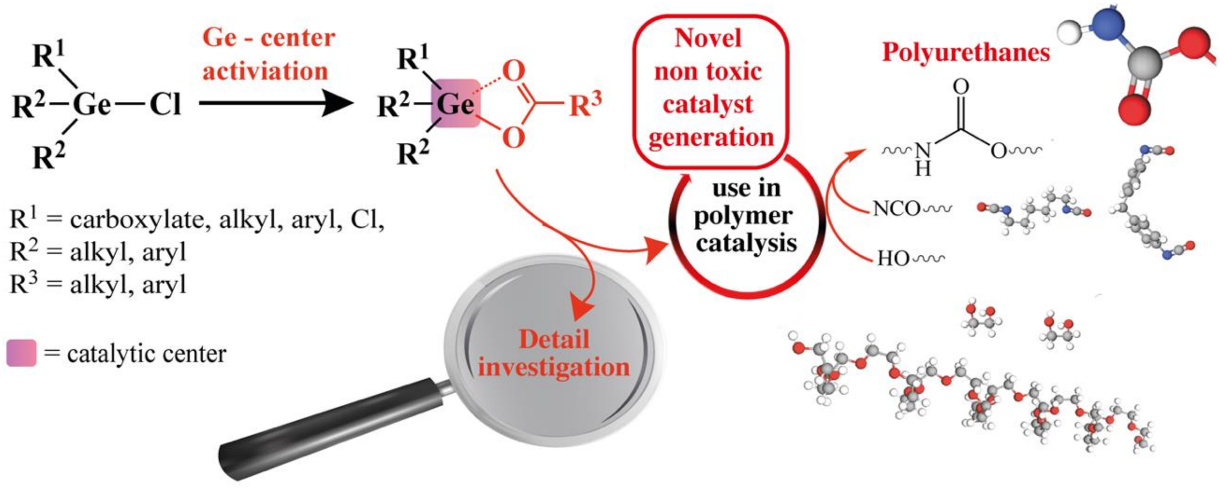
For over five decades, organotin catalysts have been used in various polyaddition reactions, e.g. in polyurethane synthesis.[1] However, since 2010, their use has been banned for several applications by the European Chemicals Agency (ECHA), e.g. as catalyst in consumer goods.[2,3] For more than two years of research work, germanium carboxylate systems were investigated as a replacement for banned tin catalysts. In April of this year, we filed our first patent application for germanium carboxylate-based catalysts.[4] In the course of this work, an overview of the path to an industrial catalyst is given. In addition, deeper insights into metalloid catalysis are presented. In particular, the synthesis of more than 20 model catalysts[5] and mechanistic studies of catalysis are emphasized. Their application in polyurethane catalysis is also demonstrated. Various commercial isocyanate and polyol building blocks are used and compared. In addition, studies on low emission catalysis and catalyst leaching have been performed.



Synthesis of the catalytically active germanium compounds and their application in polymer synthesis

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Development of smart polymers for battery safety applications based on a retro Diels-Alder reaction

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Ensuring the proper operation of battery systems in electric vehicles (EVs) has been a crucial point during last years since early detection of overheating events could avoid any undesired and irreversible damages. A potential solution to monitor the batteries temperature using thermo-responsive polymers in combination with metal oxide (MOx) sensors has been recently studied.[1]

In this work a new generation of thermo-responsive polymers focusing on the covalent attachment of thiophene molecules to a polymeric matrix by the well-known Diels-Alder (DA) reaction was developed. Exploiting the retro Diels-Alder (rDA) reaction, the original reactants can be recovered at specific temperatures. A rDA temperature higher than the boiling temperature of thiophene was measured for the studied DA reaction, allowing the release of thiophene in gas phase, easily detectable by MOx sensors.

In a first step, a model compound (TS-1) reacting a commercially available bismaleimide (BMI-689) with thiophene using a 1:1 mol ratio was synthetized. TS-1 was thermally characterized by thermogravimetric analysis (TGA) and evolved gas analysis coupled to a spectrometer (EGA-IR) to measure the rDA temperature and the gas release. A weight loss of about 20% corresponding to the cleave and release of thiophene was measured starting at 100°C (Figure 1).

In a final step, one of the maleimide groups of BMI-689 was firstly reacted with thiophene obtaining TS-2. The unreacted maleimide group was then used to attach TS-2 to a thiol-ene network containing PETMP in an UV mediated reaction to produce polymers with different thiophene content (TS-3, TS-4 and TS-5). TS-2 and the obtained polymers were also thermally characterized using the above mentioned techniques to measure the exact release of thiophene. Moreover, a sensor test setup developed by Virtual Vehicle Research GmbH was used to prove the detection of the thiophene molecules by MOx sensors after heating the polymer samples at specific temperatures.

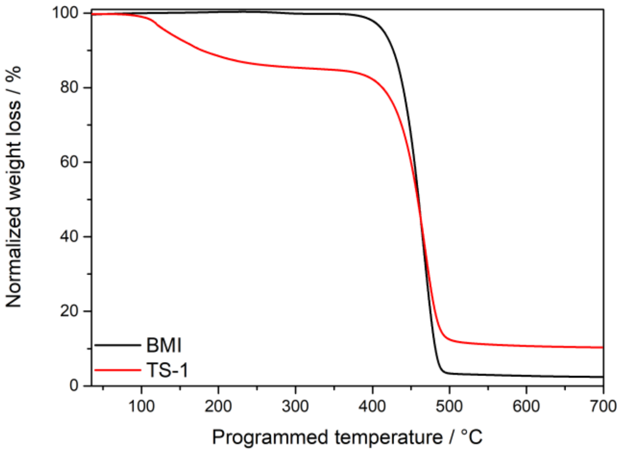

Figure 1. TGA curves of BMI and TS-1

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3D-Printed polysaccharide biomaterials: Comprehensive analysis of swelling, structural stabilization, and mechanical stability

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The advancement of 3D printing technology has significantly enhanced the development of polysaccharide-based hydrogels for applications in tissue engineering and regenerative medicine.[1] This study focuses on the fabrication and characterization of 3D-printed polysaccharide biomaterials, specifically utilizing alginate modified with tyramine and nanocellulose. Through an innovative ionic and enzyme-assisted crosslinking approach involving calcium ions (Ca^{2+}) and horseradish peroxidase (HRP) enzyme (Figure 1), we achieved structures with exceptional shape fidelity and mechanical stability. The printed materials were rigorously analyzed for their swelling behavior, structural stabilization, mechanical strength, and morphological properties. The findings demonstrate the potential of these 3D-printed polysaccharide structures to serve as robust, biocompatible, and customizable scaffolds, mimicking the properties of native tissues such as cartilage and cardiovascular tissue.[2,3]

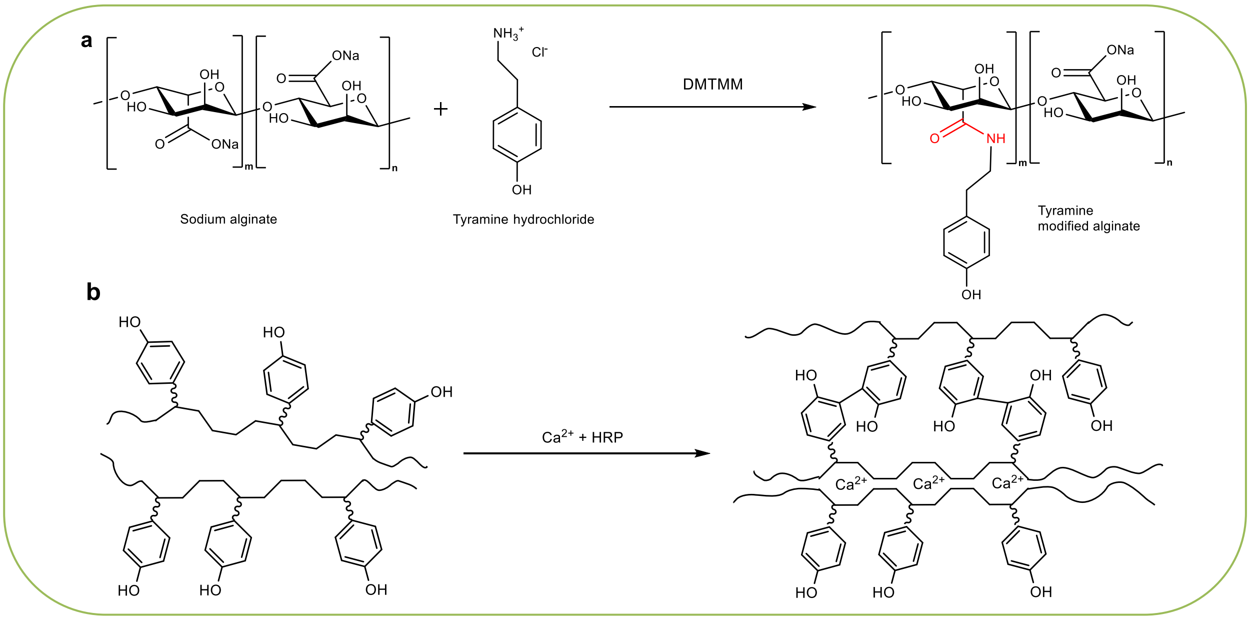

Figure 1: (a) Modification of sodium alginate with tyramine hydrochloride and DMTMM (b) ionic and enzymatic crosslinking of modified alginate

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O22

Innovative scalable synthesis of alternating acrylamide copolymers: Pathways to new applications

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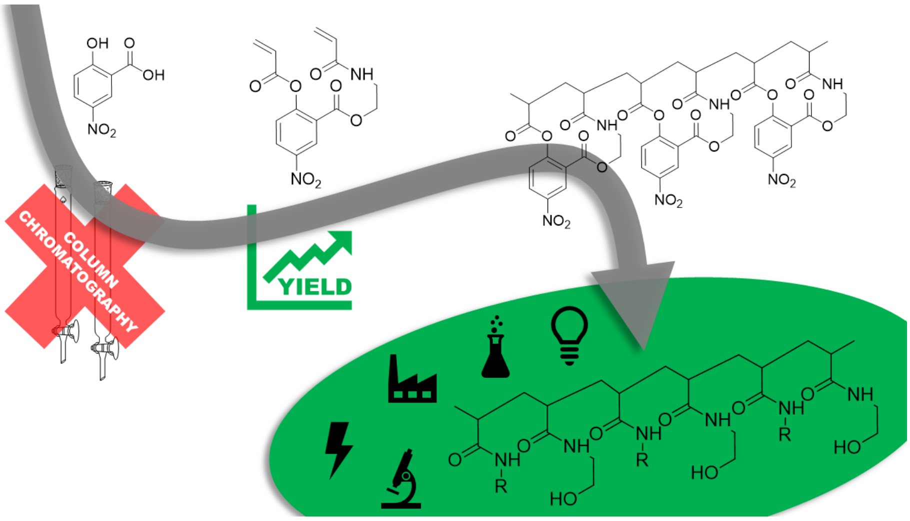
Combining different monomers to adjust the properties of polymeric materials is a standard practice in polymer chemistry and materials science. However, the sequence of monomers also significantly influences material properties. Sequence control has been a major focus since the early days of polymer science, as block or alternating architectures can offer unique properties compared to random copolymers.



Innovative Scalable Synthesis of Alternating Acrylamide Copolymers

Recently, sophisticated synthesis strategies have been developed to achieve alternating sequences using radical polymerization. However, most published methods suffer from drawbacks such as limited monomer compatibility, complex synthesis procedures, or high reagent costs. An exception is the deprotection chemistry proposed by Ouchi et al.,[1] which uses an electron-deficient salicylic acid derivative and an intramolecular reaction mechanism to produce abroad range of alternating acrylamide-based copolymers. Despite its potential, this approach lacks scalability due to multiple-column chromatography steps and low yields.

We report an improved synthesis procedure that offers high yields, straightforward work-up processes, and an innovative (photo)polymerization approach. This new method facilitates the production of a wide range of materials, supporting applications that require several grams of product. Our advancements significantly enhance the accessibility and scalability of alternating copolymer synthesis, opening new avenues for material applications.

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Covalently attachable photoacid generator in dynamic thiol-ene photopolymers for microscale manipulation of transesterification reactions

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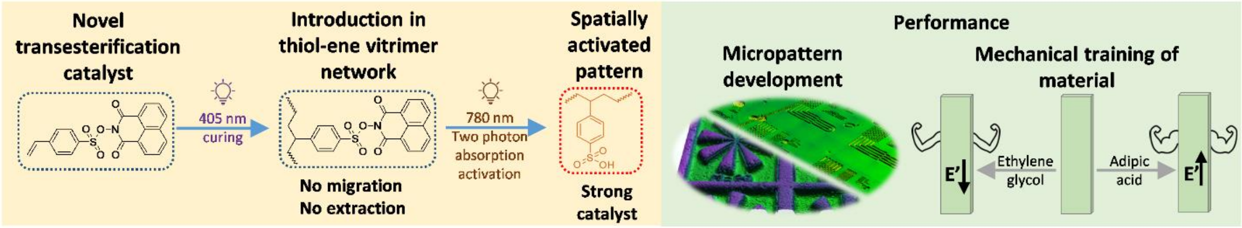
Vitrimers are dynamic polymer networks characterized by reversible covalent bond exchange reactions that allow for topology rearrangement in response to external stimuli. This temperature-dependent alteration of viscoelastic properties renders vitrimers malleable, weldable, and recyclable, making their properties modifiable via selected catalysts.[1] However, achieving spatial control in these thermo-activated systems remains challenging.[2]



Performance of novel crosslinkable photoacid generator in thiol-ene vitrimer material.

Herein, we introduce the use of photolatent catalysts to locally manipulate bond exchange reactions in vitrimers at the microscale level. We synthesize a linkable non-ionic photoacid generator, covalently attached to a thiol-click photopolymer cured at 405 nm. Upon UV-induced deprotection, a strong immobilized sulfonic acid species is released, efficiently catalyzing dynamic exchange reactions in the photopolymer. The covalent attachment of the acid prevents migration and leaching, allowing precise tuning of material properties through acid-catalyzed transesterification. As proof of concept, we inscribe positive-toned microstructures with a resolution of 5 µm in thin photopolymer films using direct two-photon absorption laser writing and subsequent depolymerization in ethylene glycol. Additionally, we demonstrate the ability to locally reprogram bulk material properties via post-modification reactions with low molecular weight alcohols and carboxylic acids, varying the Young's modulus from 3.3 MPa to 11.9 MPa. This advancement underscores the versatility of these novel catalysts in creating light-processable and transformable functional materials.[3]

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Bio-responsive polymer probes/contrast agents for dual ^{1}H/^{31}P and ^{31}P/^{19}F magnetic resonance imaging

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To enhance tissue differentiation and overall image quality, or to visualize molecular targets that are not naturally abundant, the use of contrast agents based on (super)paramagnetic metals or exogenous biocompatible probes containing X-nuclei (^{31}P, ^{19}F, ^{23}Na, etc.) can be highly advantageous in magnetic resonance imaging (MRI). In this work, a set of new types of bio-responsive polymer probes enabling dual ^{1}H/^{31}P or ^{31}P/^{19}F MRI has been developed. Specifically, three distinct types of polymer probes containing different X-nuclei or (super)paramagnetic compound have been synthesized: (i) phosphorus-containing polymer zwitterions, serving as bio-distinguishable metal-free ^{31}P MRI probes;[1] (ii) conjugates of phosphorus-containing polymer zwitterions with γ-Fe_2O_3 nanoparticles or with low-molecular-weight Fe^{3+} ions, functioning as dual ^{1}H/^{31}P probes/contrast agents;[2] and (iii) phosphorus- and fluorine-containing copolymers bearing either 5-fluorouracil derivatives or 3,5-bis(trifluoromethyl)benzylamine, designed as dual ^{31}P/^{19}F probes.

The metal-free polymer probe (i) provided a highly intense ^{31}P MR signal that was clearly distinguishable from the biological background, owing to the presence of a naturally rare phosphorothioate group (P=S). Additionally, in the presence of reactive oxygen species, the probe underwent oxidation-induced structural changes, making it a potential tool for detecting tumors or inflammation. Both types of Fe-based polymer probes (ii) exhibited very short ^{31}P and ^{1}H relaxation times; however, while those containing Fe^{3+} ions could be satisfactorily visualized by ^{1}H/^{31}P MRI, those incorporating γ-Fe_2O_3 could not be imaged due to excessively short relaxation times. The polymer probes containing both phosphorus and fluorine (iii) demonstrated optimal ^{31}P/^{19}F relaxation times, allowing for their visualization through two independent MRI modalities. Furthermore, the polymer probe containing the 5-fluorouracil moiety may also function as an anticancer prodrug.

In summary, all synthesized polymer probes incorporating phosphorus, fluorine and/or iron within their structures were successfully visualized using three distinct MRI modalities – ^{31}P, ^{19}F and ^{1}H MRI. Additionally, the probes containing P=S groups exhibited antioxidant properties, making them suitable as a sensitive MR sensor for detecting oxidative stress. Furthermore, the probe conjugated with 5-fluorouracil derivative holds potential for application in cancer treatment. Acknowledgement: This research was financially supported by the project National Institute for Cancer Research (Programme EXCELES, Project No. LX22NPO5102) - Funded by the European Union – Next Generation EU.

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Copolymerization of epoxyeugenol and bisphenol A diglycidyl ether

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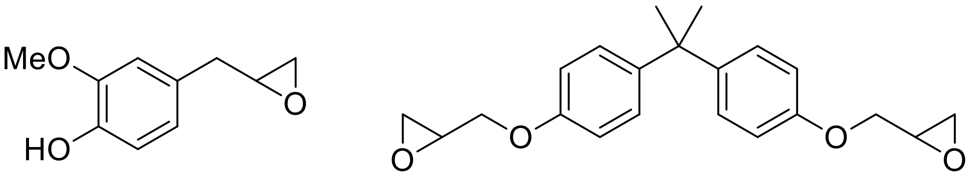
Eugenol is a liquid phenolic compound accessible from renewable resources such as clove or cinnamon, by lignin degradation or by chemical synthesis.[1] Many monomers and their corresponding polymers have been prepared from eugenol.[2] Here, we perform the epoxidation of the double bond to obtain the corresponding liquid epoxide, namely 2-methoxy-4-(oxiran-2-ylmethyl)phenol (epoxyeugenol, EE) in a single step, and test this monomer in the copolymerization with bisphenol A diglycidyl ether (DGEBA).



EE **DGEBA**

Chemical structures of the monomers under investigation.

In particular, we studied the polymerization reaction with 1-methylimidazol and with K54 as initiators using isothermal and dynamic differential scanning calorimetry (DSC) to determine activation energies for different formulations. Additionally, ^{1}H NMR studies with model compounds were performed to support the results of the DSC measurements. Furthermore, the rheological behaviour of selected formulations during the curing reaction was investigated. Lastly, the thermal properties of the resulting thermoset materials are described.

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Alternative methods for covalent cross-linking of alginates

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Plant based alginic acids ([D-ManA(β1→4)]$_m$-[L-GulA(α1→4)]$_n$) and their salts are very often used to create hydrogels for tissue culture and regeneration.[1,2] These materials are commonly gelled by multivalent ions or covalenty e.g. by (radical) polymerization of previously attached reactive functional groups. While effective, these methods often face limitations in terms of stability, biocompatibility and reversibility, giving the need for new cross-linking strategies compensating those drawbacks. Therefore, this work investigates new gelation methods for alginates, based on small molecular crosslinking agents comprising *N*-terminal glycine, which are cross-linked chemically using 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) as a coupling reagent in water (*Figure 1*). Monitoring of the gelation process via time-dependent oscillatory rheology measurements gave insights into the mechanical properties of the gels. The formed three-dimentional network of amide bonds is thought to provide higher long-term stability at physiological conditions due to limited exchange with the environment compared to ionically cross-linked hydrogels, which are prone to cation exchange. The materials used are potentially biocompatible, but the bonds formed a most likely susceptible to targeted enzymatic cleavage by esterases or proteases. This could lead to interesting properties for potential applications in tissue culture and regeneration.

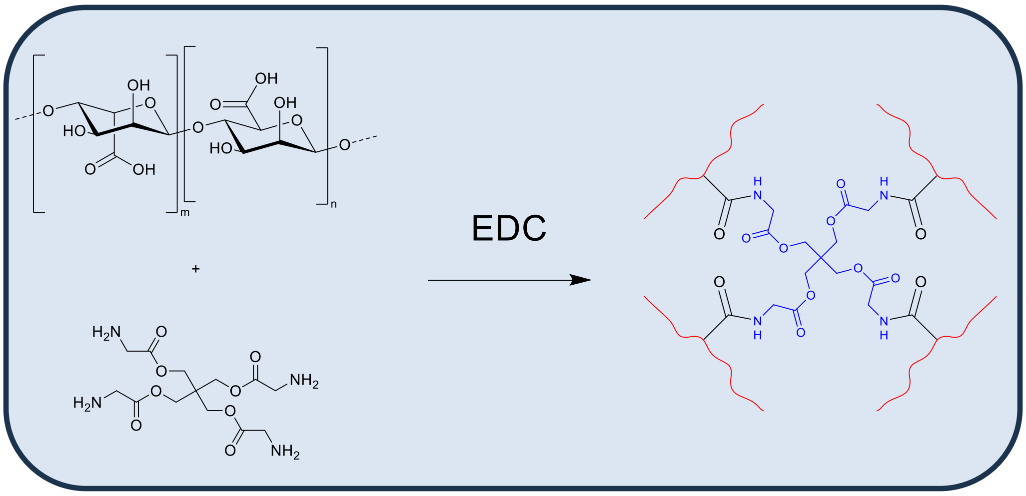

Figure 1: Covalent cross-linking of alginic acid with pentaerythritol tetrakis (glycinate) as a multifunctional spacer molecule

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Bio-based photo-initiators for UV-Nano-imprint resins

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Anja Haase, Barbara Stadlober

Materials, Joanneum Research Forschungsgesellschaft mbH
Weiz, Austria

The coating industry is making great efforts to replace fossil with renewable carbon sources. Major suppliers have recently launched entire product portfolios of UV-curable mono- and oligomers, which are partially made from bio-based raw materials. However, so far only petro-chemical aromatic photo-initiators are utilized throughout industry for starting the photo-polymerization even of such partially bio-based coatings.

Photo-initiators - typically added at a few w-% - are key components in photo-curing coating formulations. They absorb UV-radiation and generate radicals for starting the free radical polymerisation - i.e. UV-curing reaction.

We have formulated fast curing high fidelity UV-nano-imprint resins based on mono- and oligomers partially made from renewable raw materials like soy-bean oil having a bio-renewable carbon content (BRC) of more than two thirds. For photo-initiation we use e.g. 1 w-% of simple bio-based aliphatic α-ketoacids like pyruvic or ketoglutaric acid as well as corresponding esters.

Upon irradiating with wavelength $\lambda = 365$ nm the UV-curing i.e. photo-polymerisation of the investigated resins proceeds at competitive rates and to similar final photo-conversions like with conventional petro-chemical photo-initiators.

In a first application, optically variable anti-counterfeiting features have been R2R-UV-nano-imprinted into a 67 % BRC resin on 70 % post-consumer recycled (PCR) PET substrate film as well as on 98 % BRC cellophane film. Anti-reflective, water-repelling, drag reducing and potentially anti-bacterial bionic surfaces have been UV-imprinted as well in similar partially bio-based resins utilizing α-ketocarboxylic photo-initiators.

Furthermore, beyond UV-nano-imprinting – by using these new photo-initiators 100 % BRC UV-curing e.g. screen-, jet- or 3D- printing inks are within reach for a wide range of applications as soon as 100 % BRC UV-curing meth(acrylate) mono- and oligomers become commercially available.

Design and characterization of poly(dicyclopentadiene) derived hard carbons as anode materials for sodium-ion batteries

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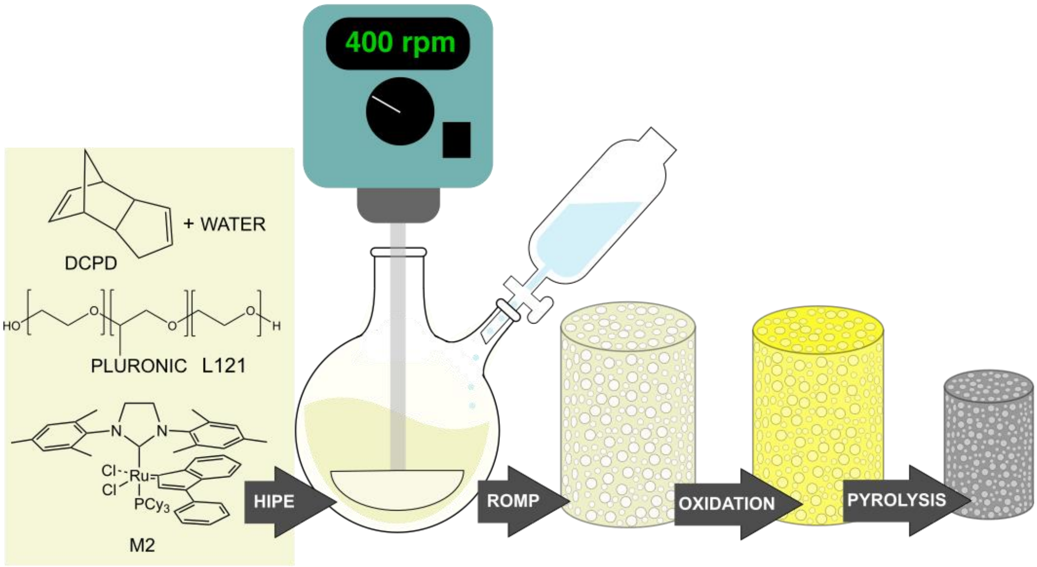
High internal phase emulsions can be used to create polymers that are characterized by their macroporous, three-dimensional structures, called polyHIPEs. These porous polymeric monoliths, with pore sizes ranging from a few microns to several hundred microns, have found use in various applications such as cell scaffolds, catalyst and reagent supports, chromatography, and filtration. Here we present a polyHIPE consisting of poly(dicyclopentadiene) (polyDCPD) synthesized by ring-opening metathesis polymerization (ROMP) of dicyclopentadiene (DCPD) present in a high internal phase emulsion.[1] The resulting polymer not only exhibits excellent mechanical properties,[2] but is also an interesting starting material for macroporous carbon foams.[3] An oxidative treatment at near room temperature is sufficient to maintain the 3D framework during pyrolysis, resulting in a conductive, porous hard carbon with yields of 35-38%. These hard carbons were further characterized as anode materials for sodium-ion batteries. Higher plateau temperature during carbonization resulted in larger nanopore diameter, which is generally associated with higher capacity. Coulombic efficiency and rate performance could be increased with a second stage CO2 activation of the hard carbon, which significantly improved cell lifetime.



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POSTER PRESENTATIONS

Preparation of di-*N*-carboxyanhydride cross-linker from glutamyl-lysine isopeptide

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The introduction of cross-links into the polymer structure affects the physical properties of the polymer networks produced, and the extent of this effect depends on the amount and distribution of the cross-linking units. To prepare cross-linked synthetic peptides by ring-opening polymerization of *N*-carboxyanhydride (NCA) monomers, a suitable di-*N*-carboxyanhydride (di-NCA) cross-linker must be used whose reactivity must match that of the monomer(s). Since glutamic acid and lysine-based α-amino acid derivatives are most commonly used for the preparation of synthetic polypeptides, we investigate the preparation of di-NCA cross-linker based on glutamyl-lysine (Glu-Lys) isopeptide.

The commonly used Fuchs-Farthing method of NCA synthesis using triphosgene proved to be unsuitable for the isopeptide, as the yield and purity of the di-NCA obtained were very low. Therefore, we used the Leuch method with various halogenating agents instead. We show that an undesired side reaction occurs with thionyl chloride, in which cyclization of the isopeptide occurs at the glutamine side of the isopeptide with the amide group, leading to the formation of a dioxopiperidine ring as the major product instead of forming the NCA group (Figure 1). By using PCl_5 or PBr_3, this side reaction can be completely avoided, leading to the formation of di-NCA.

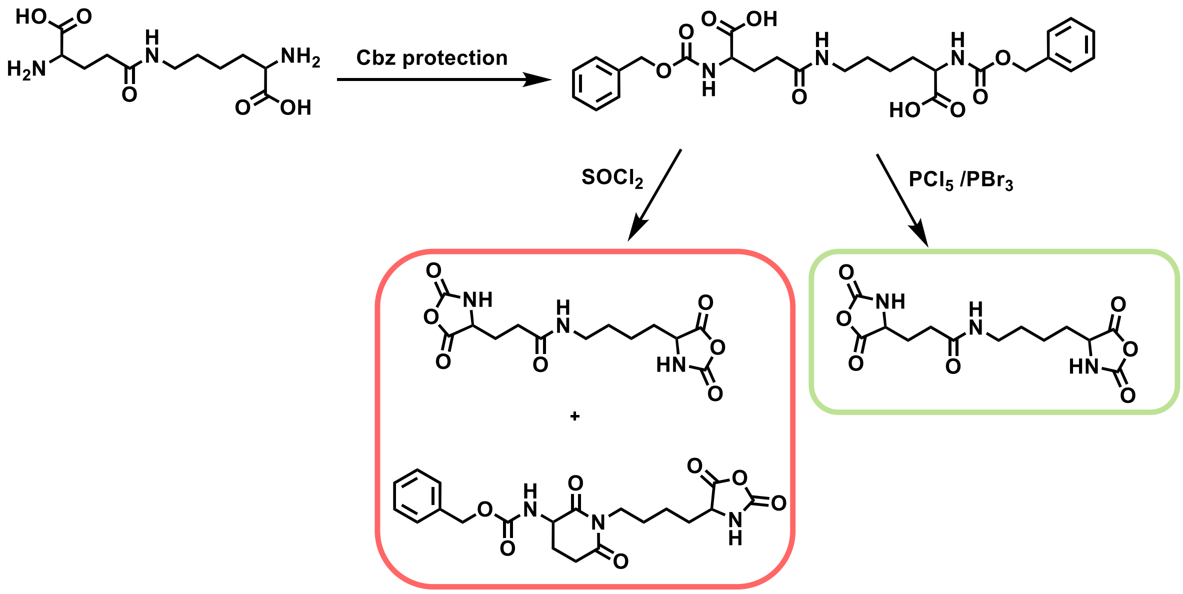

Figure 1. Preparation of Glu-Lys di-NCA using halogenating agents where an undesirable side product is formed when using thionyl chloride.

Photo-induced catalytic poly-trimerization of polyisocyanurates

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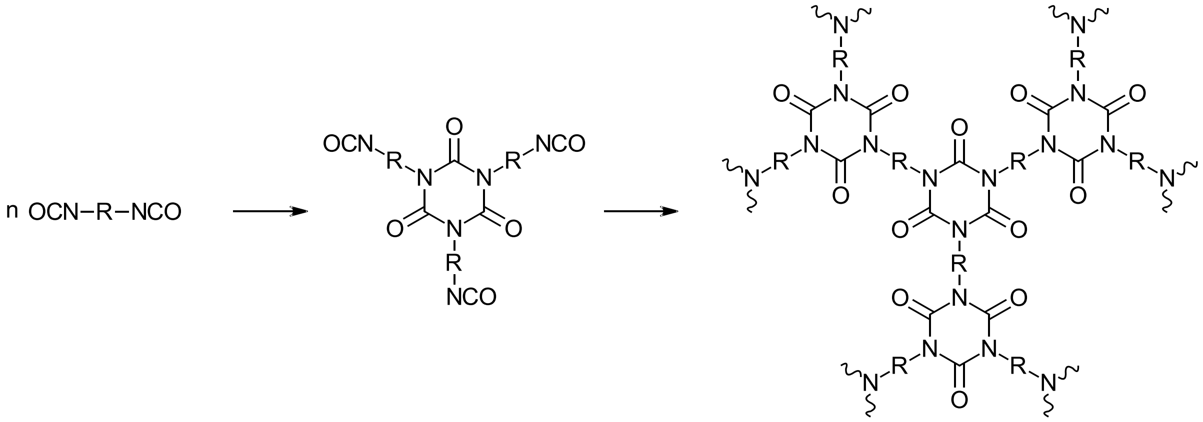
Numerous polymeric products are nowadays manufactured from isocyanates to fulfil a variety of different applications such as rigid and flexible foams, insulating materials, plastics, composites, films, sealants, coatings, and adhesives.[1,2] Isocyanate-based coatings are widely used in modern industry due to their flexibility and reduced hardness compared to other coating systems like epoxies. Especially, polyisocyanurates are seen as a promising new material class for the coating industry. Polyisocyanurates can be achieved through poly-trimerization of isocyanates or polyisocyanates and offer improved thermal and solvent stability.[1] Moreover, radiation-based curing provides efficient production conditions, due to the time- and energy-efficiency and eco-friendliness.[3] Hence, coatings by light-induced curing of polyisocyanurate would be of notable interest in the curing industry.



Poly-trimerization of multifunctional isocyanates to polyisocyanurate.

Here we want to introduce a new photo-induced and catalytic isocyanate-based system to obtain polyisocyanurates by trimerization of isocyanates. We have investigated various photocatalysts and co-catalysts and varied the curing conditions to obtain the ideal composition for the catalytic system for polyisocyanurate formation. This novel system offers new access to coatings containing isocyanates and is intended to lay the foundations for further research on the potential use of polyisocyanurates in the coating industry.

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Dynamic thioester-networks: Synthesis and characterization

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Covalent adaptable networks (CANs) are crosslinked polymer networks that exhibit dynamic bond exchange reactions at elevated temperatures allowing a topological rearrangement of the network. As a result, these polymers combine the mechanical properties and chemical stability of thermosets with the processability and recyclability of thermoplastics.[1]

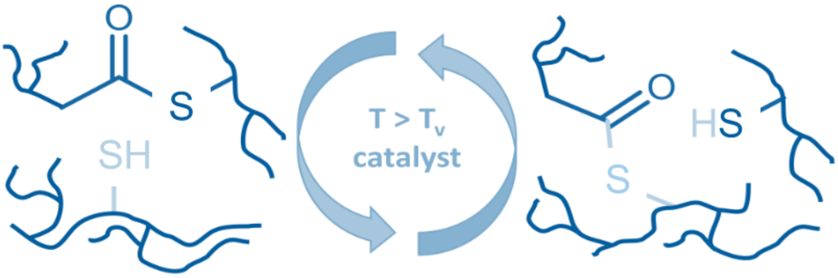

Figure 1. Thiol-Thioester exchange mechanism

In this work, the focus was placed on thiol-thioester exchange reactions (Figure 1), as these can proceed rapidly already at low temperatures in the presence of suitable catalysts, which is of particular interest for biomedical applications. In a first step, thioester- bearing vinyl monomers were synthesized to enable network formation upon exposure to visible light via a thiol-ene-click reaction. The purity of the synthesized monomers was characterized by ^{1}H- and ^{13}C-NMR spectroscopy. By using an excess of thiol moieties and adding 3 mol% tetramethylguanidine as a catalyst, a dynamic network can be prepared. TGA and DSC measurements were performed to determine the thermal stability and glass transition temperature of the network. The dynamic behavior of the network was investigated by stress-relaxation measurements at different temperatures. As expected, the characteristic relaxation time increased with decreasing temperature, following an Arrhenius trend.

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Alcohols in Lewis-base catalysed polyaddition reactions: The case of aliphatic isocyanates

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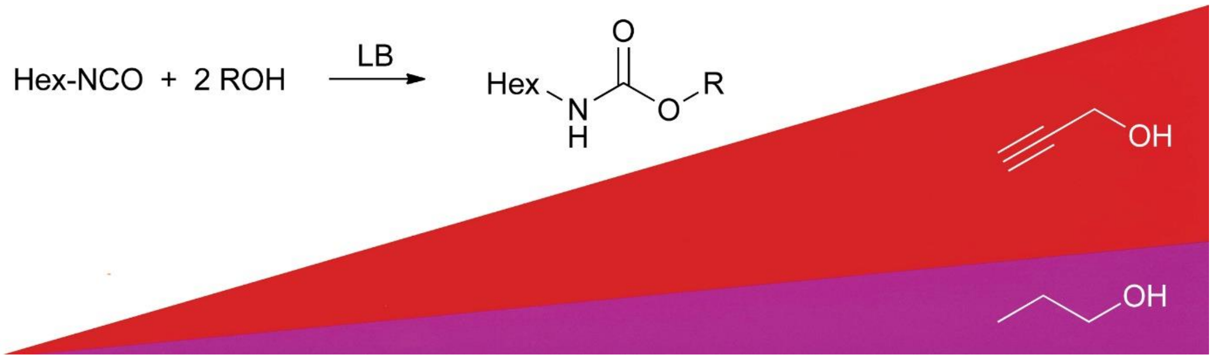
While the use of aliphatic alcohols as monomers in polyaddition reactions such as ring opening of epoxides or Michael chemistry is rather underdeveloped, alcohols are often used in the reaction with isocyanates to form poly(urethanes). For room temperature curing of aliphatic isocyanates, tin-based catalysis is still the state of the art. However, the development of fast curing tin-free formulations is an important goal for the practical application of this chemistry.[1]

In this contribution we present our results on Lewis base catalysis for the reaction of aliphatic isocyanates with alcohols at room temperature. Emphasis is placed on uncovering the role of the electronic properties of the alcohol on the rate of the reaction using different Lewis bases and dibutylin dilaureate (DBTL) as a reference catalyst. The results showed that none of the Lewis bases could compete with DBTL in catalytic activity. However, a strong dependence of the reaction rate on the acidity of the alcohol was found. More acidic alcohols (e.g. propargyl alcohol) react much faster than less acidic ones (e.g. propanol). This phenomenon is much less pronounced when DBTL is used as the catalyst.



Typical reaction under investigation; reaction conditions: 1 equiv. isocyanate, 2 equiv. alcohol, 0.01 equiv. Lewis base, room temperature, solvent free

Finally, we compare the reactivity of the alcohols in isocyanate chemistry with their reactivity with other electrohiles, namely epoxides and some Michael acceptors, and find different dependencies of the alcohols acidity on the reaction rate.[2]

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Different approaches for the fabrication of functional surfaces by introducing micro-patterns on polymers

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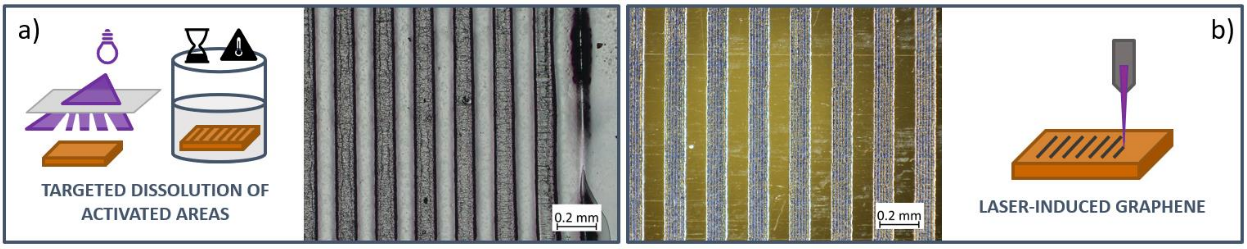
An exciting strategy to engineer material properties, such as wettability or the tribological properties of a surface, is to add micro- or nano-sized textures. Nature offers many examples where different texturing strategies (geometries and topologies) determine their functionality (e.g., gecko adhesion or lotus leave water repellency).[1]

Herein, we present one approach that combines photolithography with dynamic covalent bonds to create positive tone surface patterns. This allows for a selective dissolution using a solvent-assisted transesterification mechanism. In addition, the photoreactive resin is processable via vat photopolymerization (at 450 nm) without prior activation of the transesterification catalyst by ensuring orthogonality between the curing and the activation reaction.



Micro-sized surfaces patterns (line pattern with 100 µm thickness) fabricated a) by controlled dissolution and b) by laser induced pyrolysis

Micropatterns are then inscribed into the surface by selective exposure to visible light (405 nm). Furthermore, this work targets ways to characterize and tune selected surface properties (e.g., friction) as a function of the micropattern (e.g., size, geometry), resulting in highly versatile functional photopolymers. An alternative strategy using a UV laser to form laser-induced graphene (LIG) on the surface of a polymer film is investigated as a potential method to fabricate various surface patterns. The laser writing and subsequent transformation of the precursors into graphene through a fast photochemical and thermal pyrolytic process can be used to synthesize different LIG patterns directly. This method represents a promising way of surface functionalization as LIG-patterned surfaces have already been demonstrated to allow for tuning of the surface wettability.[2,3]

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P6

Evaluating the physical aging of PEBAX® composite hollow fiber membranes for CO_2 capture

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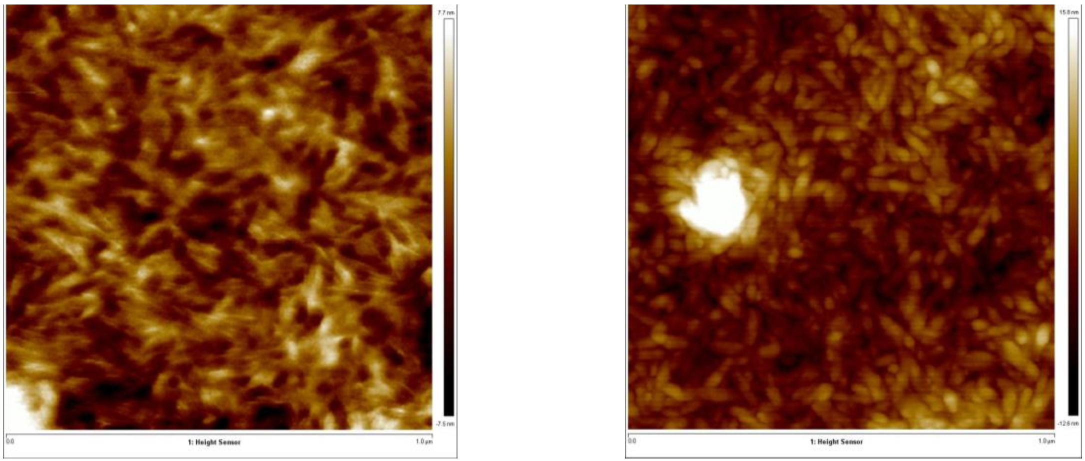
Carbon dioxide emissions have significantly increased over recent decades, largely due to flue gases from thermal power plants, contributing to global warming. Consequently, separation membrane technology for CO_2 capture has been widely explored.[1] Hollow fibers (HF) is one of the techniques utilized for carbon capture technology. Composite HF were prepared from polyacrylonitrile (PAN) porous support and coated with a separation active layer of PEBAX®, a block copolymer, largely explored for gas separation due to its PEO soft blocks, which enhance CO_2 permeability.[2] Ensuring the stability of these membranes is crucial for industrial applications.

In this study, the physical aging of PEBAX® composite HF was assessed through single gas transport properties at various pressures. It was observed that the thin layer exhibited unstable performance over time. Initially, the CO_2 permeance was 328 GPU with a CO_2/N_2 separation factor of 40 on the first day. However, after 24 days, the CO_2 permeance declined to 159 GPU and the CO_2/N_2 selectivity dropped to 14.



AFM images of fresh and old PEBAX® composite hollow fiber membrane

Small-angle X-ray scattering (SAXS) analysis did not show significant changes in crystallinity. In contrast, atomic force microscopy (AFM) was used to investigate the morphology, revealing changes in the block chains over time and suggesting a redistribution of free volume. The AFM topography revealed a structural reorganization, with a more homogeneous distribution of the blocks initially, and after 30 days, a more defined morphology.

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New debonding on-demand concepts for the repair and disassembly of adhesively-bonded structures

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Whilst polymer-based adhesives are commonly used to join different materials, they present several issues at the end-of-life of composite structures. To increase the circularity of bonded polymer parts, de-bondable on-demand adhesives present a promising method to disassemble composites in a viable timeframe, to recover the joint components without damages, and to reuse them.[1] Various external stimuli including temperature and light can be applied to induce cohesive and/or adhesive failure of bonded structures.[2] A prominent strategy involves the use of polymer networks with dynamic covalent bonds that are able to undergo bond exchange reactions as response to an external trigger. The related change in the viscoelastic properties (at elevated temperature) is then exploited for debonding processes.[3] In our recent work, we introduced a chemical amplification process in which a single photon event induced a cascade of subsequent reactions in dynamic polymer networks.[2,4] Upon UV exposure, an acid was formed, which on the one hand acted as transesterification catalyst and on the other hand removed protecting groups (t-BOC) from hydroxy functions in the polymer.[5] In the presence of the activated catalyst and the free -OH groups the network was able to undergo thermo-activated transesterification, which was demonstrated by a rapid decrease in stress relaxation. Transferring this concept to adhesives, we followed the change in the bond performance prior to and after activation of the cascade reaction as a function of selected external stimuli.

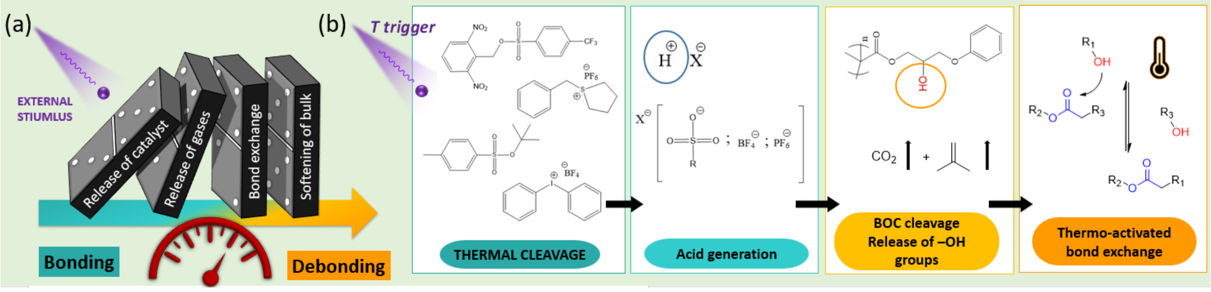

Fig. 1: General scheme of de-bond on-demand acrylate adhesive system

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P8

Surface Modification of Thiol-Ene Based Polymers for the Development of Microfluidic Systems

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In this work thiol-ene based photopolymers are surface-functionalized to create hydrophilic and hydrophobic areas for the development of microfluidic systems via photopolymerization. In this context, thiol moieties on the polymer surface are oxidized with UV-light and patterned with photomasks to yield spatially controlled hydrophilic sulfonate groups. In a further step, the remaining mercapto groups are functionalized with fluorinated acrylates via base catalyzed thiol-michael addition or with gold nanoparticles to create hydrophobic regions. The proper functionalization of the surface is monitored via contact angle measurements and X-ray photoelectron spectroscopy. Using this method microfluidic channels will be created with this method that are able to guide blood samples and detect viruses through rapid diagnostic testing.

Melting point and crystallinity of PE wax produced by different alkylaluminum co-catalysts

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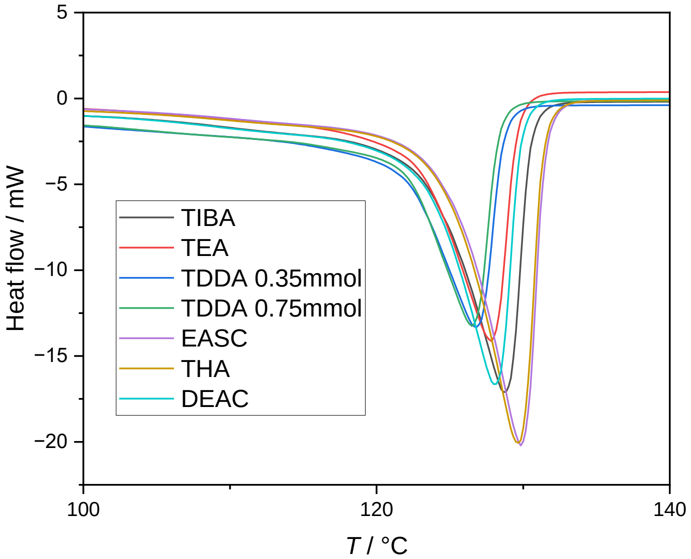
The polymerization of olefins using Ziegler-Natta catalysts is a fundamental process in the production of various plastics. These catalysts typically consist of titanium tetrachloride ($TiCl_4$), which is immobilized on an inert carrier such as magnesium chloride ($MgCl_2$) along with aluminum alkyls serving as co-catalysts. These alkyls are crucial, as they are responsible for reducing the catalyst and the formation of active centers (C*) that drive the polymerization process. The various co-catalysts influence the produced polymere in different ways, such as molecular weight, molecular weight distribution, density, melting temperature, and mechanical performance[1]. The use of different co-catalysts can result in significant variations in these properties. Factors like the type of co-catalyst, its concentration, and the reaction conditions all play crucial roles in determining the final properties of the polyethylene. In this study, the effects of different co-catalysts on PE were examined, with a focus on melting point and crystallinity.



Melting points of PE wax samples produced with different co-catalysts.

Therefore, a representative sample was selected from the array of polymers synthesized using various co-catalysts and subjected to DSC analysis. For each measurement slightly different crystallinity and melting point values were obtained. This absence of correlation between the choice of co-catalyst and the observed thermal properties suggests a relationship influenced by factors beyond the co-catalyst selection. The observed variability in crystallinity stems from differences in the molecular weights of the PE waxes. Also a potential maximum in crystallinity for PE was observed.

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Cyclic comonomers in Polyethylene – Investigating the effect of cyclic short chain branches in polyethylene

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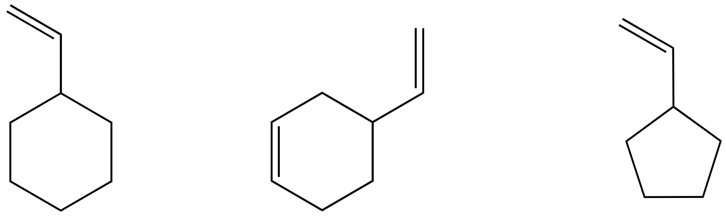
Introducing sidechains, so-called short chain branches (SCBs) into the linear backbone of polyethylene (PE) has strong effects on the polymers properties like crystallinity, density or mechanical properties. Coordinative Ziegler Natta (ZN) catalysis of ethylene produces highly linear polymer chains which are able to form solid crystalline phases. Incorporating SCBs disrupts this ability and lower crystalline fractions are formed. Alternating the structure and relative amount of SCBs may lead to tailored properties.[1] Previous studies reported that more branched comonomer structures (*iso*-hexene and *neo*-hexene) had a stronger impact on the crystallinity than the corresponding linear *n*-hexene.[2]



vinylcyclohexane 4-vinylcyclohex-1-ene vinylcyclopentane

Figure 1: Comonomers used to introduced cyclic SCBs in PE copolymers.

Advancing this research, cyclic SCBs with strong steric demand may lead to a simmilar effect. Thus, three cyclic comonomers (Figure 1) were invistigated on their possible use in PE copolymerization. The successful copolymerization of vinylcyclohexane and 4-vinylcyclhexe-1-ene with ethylene has previously been reported using various catalysts including metallocenes and ZN catalysts.[3,4] Differences in kinetic behaviour, including activation and deactivation of the catalyst during the polymerization process are compared to PE homopolymers. Furthermore, the polymers were analyzed on changes in their molecular masses and their thermal behaviour which may result from the different comonomers. The melting temperatures and melting enthalpies change as a direct result of modifications in crystallinity due to the introduced cyclic side chains. Finally, a series of copolymerizations using ethylene with *n*-butene were conducted. Therefore, more traditional copolymers were obtained to act as references with linear and shorter SCBs.

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Effects of the poly(L-lactic acid)/poly(D-lactic acid) stereocomplex on crystallisation and morphology of poly(lactic acid) materials

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The self-nucleation effect of the equimolar poly(lactic acid) stereocomplex (SC-PLA) on the crystallisation behaviour and resulting morphology of poly(DL-lactide) (PDLLA) and poly(L-lactic acid) (PLLA) matrices may lead to an improvement in material properties, in particular increased performance, which would promote the use of PLA as a bio-based and sustainable polymer[1]. In the current study, a two-step melt blending and post-annealing process has been adopted to mitigate the homocrystallisation and to produce full SC-PLA between enantiomeric poly(L-lactic acid) (PLLA) and poly(D-lactic acid) (PDLA). In order to investigate the impact of melt flow-induced precursor structures on PLA matrix nucleation, a range of processing temperatures at the SC-PLA melting threshold were selected. Differential Scanning Calorimetry (DSC) investigations of PDLLA/SC-PLA pellets with 1, 3 and 5 wt.% SC-PLA revealed that the homopolymers were partially detached from the SC-PLA crystals. This effect could be attributed to the weakening of hydrogen bonds ($-CH_3 \cdots O{=}C$) between the PLLA and PDLA segments, as well as the presence of high shear forces at temperatures above 200 °C. For Polarised Light Microscope (POM) studies, the pellets were melted at 200 °C on a heating stage and isothermally crystallised at 120 °C for 20 minutes. Subsequently, the thin films obtained were then analysed using Atomic Force Microscopy (AFM).

An increase in the weight percentage of SC-PLA resulted in the observation of self-nucleated crystallisation, accompanied by a notable rise in the number of nuclei, which ultimately led to the formation of smaller spherulites. Furthermore, the formation of shish-kebab structures (see red arrows in Figure 1. C) was observed in SC-PLA nucleated PDLLA samples across a range of processing temperatures.

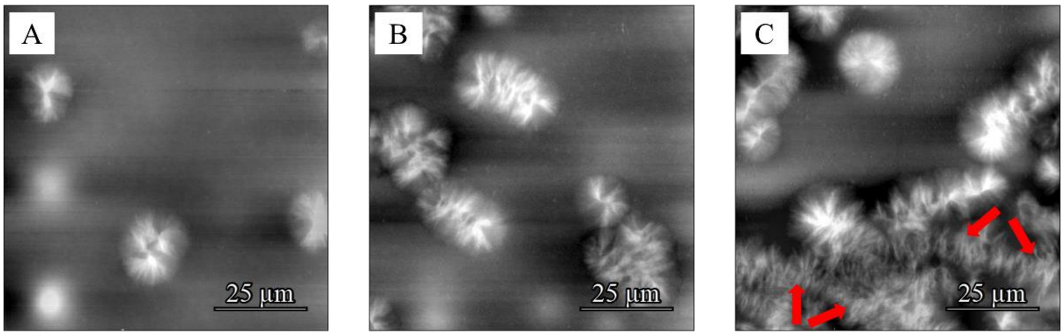

Figure 1. AFM height images of spherulites and shish-kebab structures observed in PDLLA samples extruded at 220 °C, with 1% (A), 3% (B), and 5 wt.% (C) SC-PLA. (z_{max} = 27 nm)

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Sustainably multifunctional coating design for battery safety applications based on dynamic chemistry

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In the development of battery systems, especially for electric vehicles, attention is paid not only to the efficiency and long lifespan of these energy storage systems but also to their safety. One of the critical dangers is thermal runaway, which can lead to overheating in either a local cell or the entire pack, potentially triggering thermal propagation and explosions. While recent research has focused on preventive safety techniques, such as exploring fire-proof materials for cells, safety devices for packs,[1] and managing the operation of battery packs,[2] in this work, we developed a precautionary technique by employing a thermoresponsive polymer coating that can release detectable gas at a very well-defined temperature. A thiol component acting as a tracer gas, incorporated into a polymer matrix by a click-reaction, can be cleaved and released in a gas phase upon an overheating event and detected by metal oxide (MOx) sensors, thereby triggering an alert for the harzardous condition of the batteries. Evidence for the cleavage of the thiol compound can be found in the highlighted region below, as described in Figure 1. A difference in weight loss between samples with and without tracer gas was calculated to be approximately 5 wt%, corresponding to the calculated amount of thiol compound initially inserted. Furthermore, to extend the usage cycles of the coating, a covalent adaptable network was designed for the polymer matrix, allowing it to be reprocessed after releasing the gas.

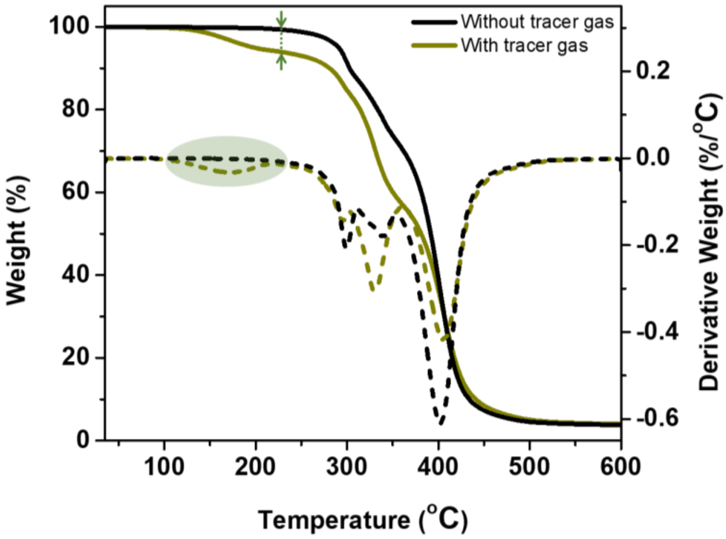

Figure 1: Thermogravimetric analysis (TGA) of the coating with and without tracer gas

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Functionalized electron-rich pyridines as initiators for the epoxy homopolymerization

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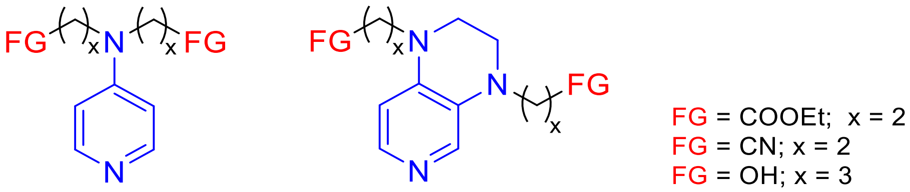
A simple and modular dialkylation of two electron-rich pyridine derivatives, namely 4-aminopyridine or 1,2,3,4-tetrahydropyrido[3,4-b]pyrazine, is achieved by aza-Michael reactions with electron-poor olefins (ethyl acrylate and acrylonitrile). Reduction of the ester groups in the ethyl acrylate-derived compounds yielded the corresponding hydroxyl-containing derivatives (Scheme 1).



Scheme 1. Electron-rich pyridines under investigation

Subsequently, the homopolymerization of phenyl glycidyl ether and an exemplary epoxy-alcohol polyaddition were carried out with the introduced compounds. As a reference, 4-dimethylaminopyridine was used. It was found that in all cases an irreversible termination of the polymerization occurred at temperatures above 100 °C. The decomposition is particularly rapid in the case of pyridine derivatives containing hydroxyl groups. In contrast, at a constant temperature of 100 °C, the latter compounds gave the fastest phenyl glycidyl ether homopolymerization and high conversions are found for all electron-rich pyridine derivatives. However, running the reaction at high alcohol concentrations at temperatures above 100°C resulted in similarly moderate conversions in all cases.[1]

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DOI: 10.1002/macp.202300299

CircEl•Paper – the search for new printed circuit boards

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The rising demand for electronics, fueled by innovations like IoT and Industry 4.0, has led to an exponential increase in the production of electronic devices. Standard printed circuit boards (PCBs), primarily made from FR4, have been the backbone of this growth. FR4 is a robust composite material known for its resilience to environmental factors like humidity, temperature fluctuations, and even fire. However, this same robustness presents significant challenges in recycling, as the material's durability makes it difficult to break down and recover valuable components.

Traditional recycling methods, such as mechanical separation, chemical dissolution, and incineration, all have significant drawbacks in terms of both economic feasibility and environmental impact. Mechanical processes often fail to fully separate the metals and plastics, chemical methods can be costly and complex, and burning, while effective in recovering metals, releases harmful emissions and destroys other materials.

To address these challenges and create more sustainable PCBs, the European Union has funded the CircEl•Paper project,[1] which is exploring innovative strategies to make PCBs greener and more environmentally friendly. Key approaches being investigated include:

1. *Substrate Material Replacement*: One of the most promising strategies is replacing FR4 with more sustainable materials, such as paper-based substrates. These materials are biodegradable and could significantly reduce the environmental footprint of PCBs.
2. *Additive Manufacturing*: Instead of traditional etching processes, which involve significant chemical waste, additive manufacturing techniques, like printing conductive and non-conductive inks, are being developed. This method can reduce waste and energy consumption.
3. *Development of New Inks*: The project is also focused on creating new types of inks that have the necessary conductive and non-conductive properties while being more environmentally friendly. This includes exploring organic materials that can replace harmful substances like Bisphenol A (BPA), a common component in traditional PCBs.

These strategies represent a significant shift towards more sustainable electronics manufacturing, with the potential to reduce the environmental impact of PCBs while maintaining their functional performance. The ongoing research under the EU-funded project CircEl•Paper could pave the way for a new class of eco-friendly PCBs, aligning with broader goals of sustainability and circular economy in the electronics industry. In this contribution we will give an introduction of the main goals and achievements of the CircEl•Paper project.

References:

1 Circular Economy Applied To Electronic Printed Circuit Boards Based On Paper (CircEl-Paper), Grant No: 101070114 Topic ID: HORIZON-CL4-2021-DIGITAL-EMERGING-01-31 DOI: 10.3030/101070114; see also: https://circelpaper.eu/

Sequential dual-curing of electron-deficient olefins and alcohols relying on oxa-Michael addition and anionic polymerization.

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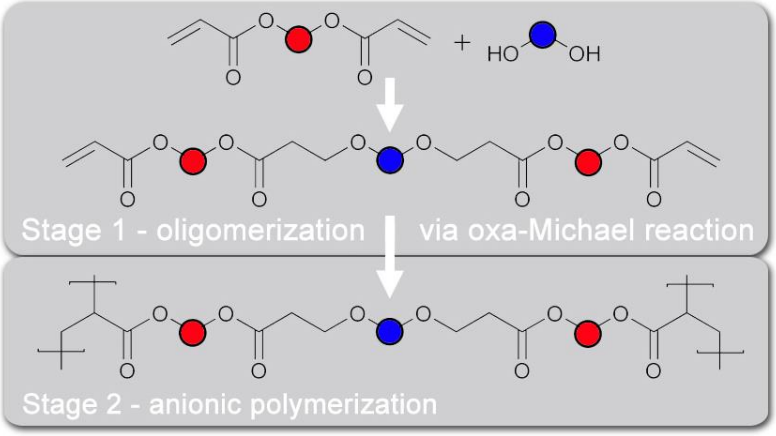
Oxa-Michael addition polymerization is an alternative to aza- or thia-Michael polymerization using potentially less expensive, less toxic and bio-sourced alcohols.[1] However, alcohols are significantly less reactive compared to their amine and thiol counterparts and require the use of tailored catalysis to react with moderately strong Michael acceptors such as acrylates. Best catalysts for the oxa-Michael polymerization of acrylates are the strong Lewis bases such as tris(2,4,6-trimethoxyphenyl)phosphine (TTMPP), or strong Brønsted bases like P_2-^{t}Bu.[2] Moreover, the reactivity of acrylates in this reaction decreases with increasing functionality further complicating the formation of polymeric networks.



Two stage copolymerization of diacrylates and diols.

Herein, we present the synthesis of polymers via the combination of oxa-Michael reactions of diacrylates and diols in stoichiometric deficiency followed by subsequent anionic polymerization of the remaining acrylate groups. TTMPP and P_2-^{t}Bu have been found to be efficient catalysts for both reactions and enable the preparation of co-polymers with varying properties (e.g. thermal stability, hardness, etc.) depending on, above all, the alcohol content. When stronger difunctional Michael acceptors such as divinyl sulfone are used, less active catalysts are sufficient to obtain a similar reactivity.[3]

References:

1 Ratzenböck, K.; Fischer, S. M.; Slugovc, C. *Monatsh. Chem.* **2023**, *154*, 443. DOI: 10.1007/s00706-023-03049-4
2 Fischer, S. M.; Kaschnitz, P.; Slugovc, C. *Catal. Sci. Technol.* **2022**, *12*, 6204. DOI: 10.1039/D2CY01335E
3 Fischer, S. M.; Schallert, V.; Uher, J. M.; Slugovc, C. *Polym. Chem.* **2023**, *14*, 1081. DOI: 10.1039/D3PY00035D

Reformable bio-based thiol-ene vitrimers for nanoimprint lithography: Enhanced covalent adaptability for adjustable surface properties

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Based on the principles of natural surfaces that are able to adaptively remodel themselves, stimuli-responsive microstructures were produced using ultraviolet (UV)-induced nanoimprint lithography. In order to achieve this, a fully bio-based dynamic thiol-ene photopolymer was synthesised through the radical-mediated addition of a trifunctional eugenol-based thiol (SH3E) to allylated linseed oil (ALELO). A bio-based eugenol phosphate ester was introduced as a transesterification catalyst, with the objective of promoting bond exchange reactions between hydroxyl and ester groups in the network. Additionally, pure eugenol was incorporated as a reactive diluent with the objective of increasing the hydroxyl group content and, consequently, accelerating the thermo-activated bond exchange reactions.

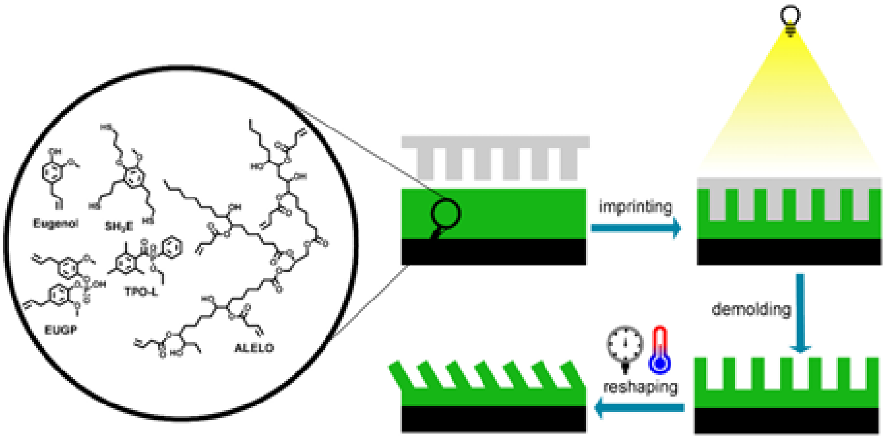

Fig. 1. Chemical structures of used monomers and general scheme of the NIL process and subsequent reshaping of microstructures

Following UV curing, the dynamic photopolymer displayed thermal stability up to 250°C and exhibited a 63% reduction in its original stress within a 62-minute period at 160°C. Films comprising micropillars with an aspect ratio of 1:2.5 were produced using nanoimprint lithography. The reflow capability of the dynamic network enabled the reorientation of the imprinted structures during thermal moulding. The imprints were subsequently analysed using 2D/3D optical microscopy, µCT imaging and static water contact angle measurements. The water contact angle was found to be between 95° and 118° depending on the orientation of the micropillars, which suggests potential applications in microfluidic devices.

Thermally-induced multi-shape-memory behavior in cross-linked EPDM and thermoplastic polyethylene blends: Potential for use as temperature indicators

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Shape memory polymers (SMPs) are smart materials that are capable of undergoing a change in shape in response to external stimuli. They have the potential to be utilised in a number of areas, including soft robotics and biomedical devices. However, the materials traditionally used are often expensive and their production processes are frequently labour-intensive. In this study, we present a versatile and cost-effective method for the preparation of SMPs using binary elastomer-thermoplastic blends. The blends were prepared by combining ethylene-propylene-diene monomer rubber (EPDM) with ultra-low density polyethylene (ULDPE), propylene-ethylene copolymer (PP-c-PE), or high density polyethylene (HDPE) as thermoplastic components.

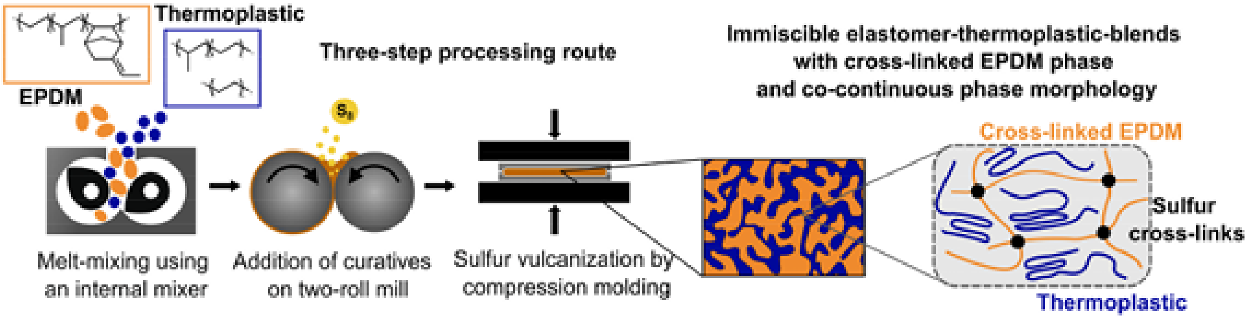

Fig. 1. Three-step processing route for the preparation of immiscible binary elastomer-thermoplastic-blends with a sulfur-cross-linked EPDM phase

Furthermore, multi-shape memory behaviour has been observed in elastomer/thermoplastic blends (40/60). Of these, blends containing ULDPE have been found to exhibit particularly promising multi-shape memory capabilities and a controllable, gradual temperature response. This behaviour is a consequence of the interaction between the cross-linked elastomer and the thermoplastic switching phase, which contains crystalline segments that melt within a temperature range of 60 to 125 degrees Celsius. The continuous shape recovery over this extensive range of temperatures renders these materials suitable for applications such as reusable test strips for temperature monitoring during transportation or for overheating protection.

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