



abiosus e.V.

Non-Profit Association for the Advancement of Research on Renewable Raw Materials

9th Workshop on Fats and Oils as Renewable Feedstock for the Chemical Industry

**March 19-21, 2017
Karlsruhe, Germany**

in Cooperation with

Agency of Renewable Resources (FNR)



Scientific and Organizing Committee

Ursula Biermann, University of Oldenburg, Oldenburg, Germany

Norbert Holst, Agency of Renewable Resources (FNR), Gülzow, Germany

Michael A. R. Meier, Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany

Jürgen O. Metzger, *abiosus* e.V. and University of Oldenburg, Oldenburg, Germany

Acknowledgement

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German Bundestag

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Program

Lectures and Posters

Sunday, March 19, 2017

Registration

Registration will be open from 15:00 - 19:00

15.45 **Welcome and Opening**

Jürgen O. Metzger, *abiosus* e.V.

Michael A. R. Meier, KIT

16.00 – 17.30 *First Session*

Chair: Michael A. R. Meier

16.00 – 16.30 **Dendrorefining: sustainable chemistry with wood based products (M)**

L1 Markus Antonietti, Max Planck Institute of Colloids and Interfaces, Potsdam, Germany

16.30 – 17.00 **Next-generation block polymers from renewable feedstocks (M)**

L2 Marc Hillmyer, University of Minnesota, Department of Chemistry, Minneapolis, MN, USA

17.00 – 17.30 **Biosynthesis and accumulation of lipids in novel bacterial isolates from the desert in Saudi Arabia (M)**

L3 Alexander Steinbüchel,^{1,2} Annika Röttig,¹ Philippa Hauschild,¹ Mohamad H. Madkour,^{2,1} Institut für Molekulare Mikrobiologie und Biotechnologie, Universität Münster, Germany, ² Department of Environmental Science, King Abdulaziz University, Jeddah, Saudi Arabia

17.30 – 20.30 **Poster Session and Opening Mixer**

Posters will be displayed until the end of the workshop

(M) Main Lecture 30 min. including discussion

(D) Discussion Lecture 20 min including discussion

Monday, March 20, 2017

9.00 – 10.30 *First morning session*

Chair: Ivan V. Kozhevnikov

9.00 – 9.30 **Catalysis for introducing, removing and swapping functional groups (M)**

L4 Bill Morandi, Max-Planck-Institut für Kohlenforschung, Mülheim an der Ruhr, Germany

9.30 – 9.50 **Intensifying homogeneous catalysed reactions with fatty compounds (D)**

L5 Andreas J. Vorholt, Thomas Seidensticker, Arno Behr, Tom Gaide, Jens Dreimann, Institute Technische Chemie, Faculty for bio- & chemical engineering, TU Dortmund, Germany

9.50 – 10.10 **One pot synthesis of hydroxylated or amino-hydroxylated triglycerides (D)**

L6 Frédéric Hapiot, Théodore Vanbésien, Eric Monflier, Univ. Artois, CNRS, Centrale Lille, ENSCL, Univ. Lille, UMR 8181, Unité de Catalyse et de Chimie du Solide (UCCS), Lens, France

10.10 – 10.30 **A modified Wacker Oxidation process: efficient oxo-functionalization of fatty acid derivatives for the synthesis of renewable basic chemicals and polymers (D)**

L7 Marc v. Czapiewski, Michael A. R. Meier, Karlsruhe Institute of Technology (KIT), Institute of Organic Chemistry (IOC), Materialwissenschaftliches Zentrum MZE, Karlsruhe, Germany

10.30 – 11.00 **Coffee break**

11.00 – 12.30 *Second morning session*

Chair: Kurt Faber

11.00 – 11.30 **In situ combination of enzymatic decarboxylation and olefin metathesis for the synthesis of bio-based diols (M)**

L8 Robert Kourist, Samiro Bojarra, Álvaro Gomez-Baraibar, Ruhr-Universität Bochum, Bochum, Germany

11.30 – 11.50 **First direct co-polymerization of internal unsaturated fatty acid esters with α -olefins (D)**

L9 Andre Fleckhaus, Mark Rüschen. Klaas, University of Applied Sciences Emden-Leer, Emden, Germany

- 11.50 – 12.10 **Linear selective isomerization / hydroformylation for ω -functionalization of fatty acid methyl esters (D)**
L10 Tom Gaide, Jonas Bianga, Arno Behr, Andreas J. Vorholt, Lehrstuhl Technische Chemie, Technische Universität Dortmund, Dortmund, Germany
- 12.10 – 12.30 **Properties of plant oil derived polyesters and thereof catalytically obtained polyethers (D)**
L11 Patrick-Kurt Dannecker¹, Ursula Biermann², Jürgen O. Metzger², Michael A. R. Meier¹, ¹ Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany, ² abiosus e.V. and University of Oldenburg, Oldenburg, Germany
- 12.30 – 14.00 **Lunch break**
- 14.00 – 15.30 *First afternoon session*
Chair: Henri Cramail
- 14.00 – 14.30 **Synthesis of chemicals from renewable feedstocks catalysed by heteropoly acids (M)**
L12 Ivan V. Kozhevnikov, Department of Chemistry, University of Liverpool, UK
- 14.30 – 14.50 **A new core of dendrimers from glycerol by nucleophilic addition of glycerol to acrylic compounds (D)**
L13 Frédéric Nadeau, Michèle Sindt, Nicolas Oget, Laboratoire de Chimie et Physique-Approche multiéchelle des Milieux Complexes (LCP-A2MC), Université de Lorraine, Metz, France
- 14.50 – 15.10 **Oligomerization of glycerol carbonate esters (D)**
L14 Romain Valentin, Marine Bonhomme, Christopher Wallis, Zéphirin Mouloungui, Unité de Chimie Agro-Industrielle, UMR1010 INRA/INP-ENSIACET, Toulouse, France
- 15.10 – 15.30 **Next generation sugar-based vegetable oil structuring agents: synthesis, assembly, morphological evaluation and applications (D)**
L15 Malick Samateh,^{1,2} Sai Sateesh Sagiri,¹ Daisy Pulido,¹ Nannette Hernandez,¹ Riliwan Sanni,¹ George John*^{1,2}, ¹Department of Chemistry & Center for Discovery and Innovation (CDI), the City College of New York, New York, ² Ph.D. Program in Chemistry, the Graduate Center of the City University of New York, New York
- 15.30 – 16.00 **Coffee break**

- 16.00 – 17.30 *Second afternoon session*
- Chair: Bill Morandi*
- 16.00 – 16.30
L16 **Oleochemical carbonates from CO₂ and renewables (M)**
Thomas Werner, Hendrik Büttner, Johannes Steinbauer, Christoph Wulf
Leibniz-Institut für Katalyse e.V., Rostock, Germany
- 16.30 – 16.50
L17 **Catalytic transesterification of organic carbonates with bio-based building blocks (D)**
Laurent Plasseraud, Gilles Boni, Sylvie Pourchet, Institut de Chimie Moléculaire (ICMUB), Université de Bourgogne Franche-Comté, Dijon, France
- 16.50 – 17.10
L18 **Synthesis and properties of new cross-linked bio-based aliphatic polycarbonates (D)**
Pierre-Luc Durand,^{1,2} Guillaume Chollet,³ Etienne Grau,^{1,2} Henri Cramail^{1,2};
¹ Univ. Bordeaux, LCPO, Pessac, France; ² CNRS, LCPO, Pessac, France;
³ ITERG, Pessac, France
- 17.10 – 17.30
L19 **Life cycle assessment of bio-based, waterborne PU Adhesives for fast industrial bonding processes (D)**
Daniel Maga¹, Martin Melchior², Hartmut Henneken³, Andreas Taden⁴
¹ Fraunhofer UMSICHT, Oberhausen, Germany; ² Covestro Deutschland AG, Leverkusen, Germany; ³ Jowat SE, Detmold, Germany; ⁴ Henkel AG & Co. KGaA, Düsseldorf, Germany
- 19.30 *Conference Dinner*
- Achat Plaza Karlsruhe**

Tuesday, March 21, 2017

9.00 – 10.30 *First morning session*

Chair: Alessandro Gandini

9.00 – 9.30 **Non-Isocyanate route to fatty acid-based polyurethanes: bulk and water-borne processes (M)**

L20 Henri Cramail,^{1,2} Océane Lamarzelle,^{1,2} Estelle Rix,^{1,2} Etienne Grau,^{1,2} Guillaume Chollet³; ¹ Université de Bordeaux, Laboratoire de Chimie des Polymères Organiques, Pessac, France; ² CNRS, Laboratoire de Chimie des Polymères Organiques, Pessac, France; ³ ITERG, Pessac, France

9.30 – 9.50 **Latex-based pressure sensitive adhesives using conjugated linoleic acid (D)**

L21 Marc A. Dubé, Stéphane Roberge, University of Ottawa, Ottawa, Canada

9.50 – 10.10 **Optimization studies on viscosity and thermomechanical properties of highly methacrylated bio-based resins (D)**

L22 Arvin Z. Yu, Dean C. Webster, North Dakota State University, Coatings and Polymeric Materials Department, Fargo, North Dakota, USA

10.10 – 10.30 **New type biobased difunctional monomers: epoxidized acrylated derivatives of castor oil (D)**

L23 Gökhan Çaylı,¹ Adem Çınarlı,² Demet Gürbüz,²; ¹ Istanbul University Department of Engineering Sciences, Istanbul, Turkey; ² Istanbul University Department of Chemistry Sciences, Istanbul, Turkey

10.30 – 11.00 **Coffee Break**

11.00 – 12.30 *Second morning session*

Chair: Christophe Detrembleur

11.00 – 11.30 **Diels-Alder and cationic polymerization of monomers derived from plant oils and furans (M)**

L24 Alessandro Gandini, University of Sao Paulo, Sao Paulo, Brasil

11.30 – 11.50 **Unfold innovation with original lipidic hyperbranched polyesters (D)**

L25 Caroline Hillairet,¹ Jérôme Le Nôtre,¹ Blandine Testud,² Etienne Grau,² Daniel Taton,² Henri Cramail,² Didier Pintori³; ¹ SAS PIVERT, Compiègne, France; ² Bordeaux University – CNRS, Bordeaux, France; ³ ITERG, Bordeaux, France

- 11.50 – 12.10 **Structure property relationship of lignin inspired phenolic polyethers synthesized via ADMET (D)**
L26 Andrea Hufendiek, Laetitia Vlamincx, Sophie Lingier, Filip E. Du Prez, Department of Organic and Macromolecular Chemistry, Polymer Chemistry Research Group, Ghent University, Ghent, Belgium
- 12.10 – 12.30 **Unconventional renewable raw materials as sources for lubricants (D)**
L27 Gunther Krafft, Rolf Luther, FUCHS SCHMIERSTOFFE GMBH, Mannheim, Germany
- 12.30 – 14.00 **Lunch break**
- 14.00 – 16.00 *Afternoon session*
Chair: Robert Kourist
- 14.00 – 14.30 **Biocatalytic cascades for the synthesis of alkenes, dienes and amino acids from fatty acids (M)**
L28 A. Dennig,^{a,b} A. Dordic,^{a,b} S. Gandomkar,^b T. Haas,^c M. Hall,^b M. Kuhn,^b S. Kurakin,^{a,b} M. Plank,^b E. Tassano,^b A. Thiessenhusen,^c S. Velikogne,^b C. Winkler,^b Kurt Faber,^b; ^a Austrian Centre of Industrial Biotechnology c/o ^b Department of Chemistry, University of Graz, Graz, Austria; ^c Evonik Creavis, Marl, Germany
- 14.30 – 15.00 **Oils and CO₂, a promising combination for designing insulating foams and high performance coatings (M)**
L29 Christophe Detrembleur¹, M. Alves^{1,2}, B. Grignard¹, S. Gennen¹, S. Panchireddy, R. Méreau², T. Tassaing², C. Jérôme¹, ¹ Center for Education and Research on Macromolecules (CERM), CESAM Research Unit, Université de Liège, Chemistry Department, Liège, Belgique; ² Institut des Sciences Moléculaires, UMR 5255 CNRS, Université Bordeaux, Talence, France
- 15.00 – 15.30 **New high-value chemicals, polymers and materials from renewable resources: a contribution to the development of the biorefinery concept (M)**
L30 Armando Silvestre, CICECO-Aveiro Institute of Materials and Department of Chemistry, University of Aveiro, Aveiro, Portugal
- 15.30 **Poster Award and Closing Remarks**
Best Poster Award
Award committee (Markus Dierker, Armando Silvestre, Alexander Steinbüchel, Thomas Werner)
- 15.45 **End of Workshop**

Posters

- P1 **Transesterification of wild chestnut oil**
Călin Jianu, Ionel Jianu
Department of Food Technology, Faculty of Food Processing Technology, Banat's University of Agricultural Sciences and Veterinary Medicine, Timișoara, Romania
- P2 **Vegetable waxes with directed hydrophilicity/hydrophobicity**
Călin Jianu, Ionel Jianu
Department of Food Technology, Faculty of Food Processing Technology, Banat's University of Agricultural Sciences and Veterinary Medicine, Timișoara, Romania
- P3 **Graphene Based Heterogeneous Acid Catalysts for the Production of Biodiesel from Waste Cooking Oil**
Reena D Souza,^{1,2} Tripti Vats,² Amit Chattree,¹ Prem Felix Siril²
¹ SHIATS, Allahabad, Uttar Pradesh, India, ² IIT Mandi, Mandi, Himachal Pradesh, India
- P4 **Synthesis of Furyl-Containing Bisphenol Based on Chemicals Derived from Lignocellulose and its Utilization for Preparation of Clickable (Co) Poly(arylene ether sulfone)s**
Samadhan S. Nagane, Sachin S. Kuhire, Prakash P. Wadgaonkar
CSIR-National Chemical Laboratory, Pune, India
- P5 **SYNTHESIS OF EPOXIDIZED SOYBEAN OIL BASED POLYOLS AND EXAMINATION OF THEIR FLAME RETARDANCY**
Deniz YERLEŞTİ, Tarik EREN
Yıldız Technical University, Istanbul, Turkey
- P6 **Synthesis of new bio-sourced polymers starting from glycerol-based divinylglycol**
Léa Bonnot,^{1,2,3} Etienne Grau,^{1,2,3} Henri Cramail^{1,2,3}
¹ Univ. Bordeaux, LCPO, UMR 5629, Pessac, France, ² CNRS, LCPO, UMR 5629, Pessac, France, ³ ENSCBP, France
- P7 **Fatty acid-based Vinylogous Urethane Vitrimers: Controlling the Viscoelastic Properties via Catalysis**
M. A. Drosbeke, W. Denissen, J. M. Winne, F. E. Du Prez
Department of Organic and Macromolecular Chemistry, Polymer Chemistry Research Group and Laboratory, Ghent University, Ghent, Belgium
- P8 **Tandem hydroformylation/hydrogenation of natural oil derived substrate and catalysts recycling through crystallisation**
Marc RL Furst, Thomas Seidensticker, Tom Gaide, Vedat Korkmaz, Andreas J Vorholt,
TU Dortmund, Lehrstuhl für Technische Chemie, Dortmund, Germany
- P9 **Photopolymerization of acrylated methyl ricinoleate**
Pinar Cakir¹, **Gokhan Cayli**²
¹ Faculty of Engineering and Architecture, Department of Biomedical Engineering, Istanbul Arel University, Istanbul, Turkey, ² Faculty of Engineering Department of Engineering Sciences, Istanbul University, Istanbul, Turkey

- P10 **Facile Synthesis Of Pristine Graphene-Palladium Nanocomposites With Extraordinary Catalytic Activities Using Swollen Liquid Crystals.**
Tripti Vats, Sunil Dutt, Raj Kumar, Prem Felix Siril
 Indian Institute of Technology Mandi (IIT Mandi), Mandi, INDIA
- P11 **New Bio-Based Polyurethane Organogelators: Synthesis and Characterization**
Sachin S. Kuhire, Prakash P. Wadgaonkar
 CSIR-National Chemical Laboratory, Pune, India
- P12 **Synthesis of Simple Chemical Building Blocks from Algae Oil**
Dennis Pinggen, Nele Klinkenberg, Julia Zimmerer, Stefan Mecking,
 University of Konstanz, Konstanz, Germany
- P13 **Combination of different methods of liquid chromatography for the analysis of glycerol products oxidation**
AMOUREUX Mathilde,^{a,b,c} MOULOINGUI Zéphirin,^{a,b,c*}
^a Université de Toulouse, INPT-ENSIACET, LCA (Laboratoire de Chimie Agro-Industrielle), ENSIACET, Toulouse, France, ^b INRA, UMR 1010CAI, Toulouse, France, ^c LabCom C2R-BioNut (Laboratoire Commun Chimie du Carbone Renouvelable pour la Biofertilisation et la Nutrition des Plantes), LCA & Agronutrition, Toulouse, France
- P14 **Synthesis and properties of new functionalized bio-based estolides**
Hélène Méheust,^{1,2} Guillaume Chollet,³ Etienne Grau,^{1,2} Henri Cramail^{1,2*}
¹ Univ. Bordeaux, LCPO, UMR 5629, Pessac, France, ² CNRS, LCPO, UMR 5629, Pessac, France, ³ ITERG, Pessac, France
- P15 **First Row Transition Metal Catalyzed One-Pot Oxidative Cleavage of Unsaturated Fatty Acids**
Jianming Chen, Joren Dorresteyn, Marc de Liedekerke, Matthias Otte, Robertus J. M. Klein Gebbink
 Organic Chemistry and Catalysis, Debye Institute for Nanomaterials Science, Utrecht University, Utrecht, the Netherlands
- P16 **Polymerization of Epoxidized Soybean Oil with Carboxyl Functionalized Boron Esters**
Gökhan Çaylı,¹ Pınar Çakır Hatır,²
¹ Istanbul University Department of Engineering Sciences, Istanbul, Turkey, ² Istanbul Arel University Department of Biomedical Engineering, Istanbul, Turkey
- P17 **CALB as an efficient catalyst for a greener production of biosurfactants : screening of the main influent parameters and optimization**
Dounia Arcens, Henri Cramail, Frédéric Peruch, Etienne Grau, Stéphane Grelier
 Laboratoire de Chimie des Polymères Organiques (LCPO, UMR 5629), Pessac, France

- P18 **Modification of Cellulose via Ugi 5CR in CO₂ switchable solvent**
K.N. Onwukamike,^{a,b} S. Grelier,^b E. Grau,^b H. Cramail,^{b,*} M.A.R. Meier^{a,*}
^a Materialwissenschaftliches Zentrum MZE, Institute of Organic Chemistry (IOC), Karlsruhe Institute of Technology (KIT) Karlsruhe, Germany; ^b Laboratoire Chimie Polymères Organiques, Université de Bordeaux/ Ecole Nationale supérieure de Chimie, de Biologie & de Physique, Pessac, France
- P19 **Chain Multiplication of Fatty Acids**
Manuel Häußler, Timo Witt, Stefan Mecking
 Chair of Chemical Materials Science, Department of Chemistry, University of Konstanz, Konstanz, Germany
- P20 **Organocatalyzed non-isocyanate polyurethane (NIPU) coatings from bio-based cyclic carbonates**
Arvin Z. Yu, Raul Setien, James Docken, Dean C. Webster
 North Dakota State University, Coatings and Polymeric Materials Department, Fargo, North Dakota, USA
- P21 **Tunable polymer films obtained from allylated lignin and plant oils via cross-metathesis**
Lena Charlotte Over, Michael A. R. Meier,^{*}
 Laboratory of Applied Chemistry, Institute of Organic Chemistry (IOC), Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany.
- P22 **Multi-enzyme cascades for the derivatization of bio-based molecules**
Samiro Bojarrá, Marius Grote, Alvaro Gomez Baraibar, Robert Kourist
 Department of Biology and Biotechnology, Ruhr-University Bochum, Germany
- P23 **From Plant to Plastic: Synthesis of renewable polyamide-15 building block from erucic acid**
D. Franciolus, F. van der Klis, R. Blaauw
 Wageningen Food & Biobased Research, Wageningen, the Netherlands
- P24 **From unsaturated fatty acids to linear dicarboxylic acids: A direct access by isomerizing hydroxycarbonylation**
Verena Goldbach,¹ Laura Falivene,² Lucia Caporaso,³ Luigi Cavallo,² Stefan Mecking¹
¹ University of Konstanz, Konstanz, Germany, ² King Abdullah University of Science and Technology, Thuwal, Kingdom of Saudi Arabia,
³ University of Salerno, Fisciano, Italy
- P25 **Fatty acid-modified cyclodextrins as mass transfer promoters for aqueous rhodium catalyzed hydroformylation**
Aurélien Coccq, Hervé Bricout, Cyril Rousseau, Sébastien Tilloy, Eric Monflier
 Univ. Artois, CNRS, Centrale Lille, ENSCL, Univ. Lille, UMR 8181, Unité de Catalyse et de Chimie du Solide (UCCS), Lens, France
- P26 **SLE diagram for a high oleic palm oil based fatty acid mixture at low saturated content**
S. Dasgupta, C. Glaser, P. Ay
 Chair of Mineral Processing, Brandenburg University of Technology, Cottbus-Senftenberg, Germany

- P27 **Controlled Radical Polymerization of Polymeric Linoleic Acid with Styrene and Pentafluorostyrene**
Abdulkadir Allı,^{1*} Sema Allı,²
¹ Düzce University, Department of Chemistry, Düzce, Turkey; ² Düzce University, Department of Polymer Engineering, Düzce, Turkey
- P28 **Synthesis and Characterization of Graft Copolymer Based Polymeric Fatty Acid Using Free Radical Polymerization and the Ring Opening Polymerization**
Abdulkadir Allı,¹ Sema Allı,^{2*}
¹ Düzce University, Department of Chemistry, Düzce, Turkey; ² Düzce University, Department of Polymer Engineering, Düzce, Turkey
- P29 **One Pot Synthesis of Oil-Based Graft Copolymers by Using ATRP and ROP**
Abdulkadir Allı,¹ Sema Allı,²
¹ Düzce University, Department of Chemistry, Düzce, Turkey; ² Düzce University, Department of Polymer Engineering, Düzce, Turkey
- P30 **One-Step Synthesis of Poly(linoleic acid)-g-Poly(N-isopropylacrylamide)-g-Poly(D,L-lactide) Graft Copolymers**
Abdulkadir Allı,¹ Sema Allı,²
¹ Düzce University, Department of Chemistry, Düzce, Turkey; ² Düzce University, Department of Polymer Engineering, Düzce, Turkey
- P31 **New Partially Bio-based Epoxy Thermosets Starting from Cashew Nut Shell Liquid: Synthesis and Thermomechanical Properties**
Amol B. Ichake,^{1,2} Etienne Grau,¹ Prakash P. Wadgaonkar,² Henri Cramail¹
¹ Laboratoire de Chimie des Polymères Organiques (LCPO), ENSCBP-Bat A 16, Pessac, France; ² Polymer Science and Engineering Division, CSIR-National Chemical Laboratory, Pune, India
- P32 **Eco-friendly aerobic oxidation of α -pinene catalyzed by homogeneous and heterogeneous Mn catalysts**
Y. S. Raupp,¹ C. Yildiz,² W. Kleist,² M. A. R. Meier,^{1,*}
¹ Institute of Organic Chemistry, Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany; ² Institute for Chemical Technology and Polymer Chemistry, Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany
- P33 **A dual catalysis approach: Selective conversion of multiunsaturated fatty acids via hydrogenation and isomerizing alkoxyacylation**
Sandra K. Hess, Verena Goldbach, Natalie S. Schunck, Stefan Mecking
University of Konstanz, Konstanz, Germany
- P34 **Highly efficient Tsuji-Trost allylation of biobased phenols catalyzed by Pd-nanoparticles in water**
Baptiste Monney,¹ Audrey Llevot,¹ Ansgar Sehlinger,¹ Silke Behrens,² Michael A. R. Meier¹
¹ Karlsruhe Institute of Technology (KIT), Institute of Organic Chemistry (IOC), Karlsruhe, Germany; ² Institute of catalysis Research and Technology, Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany

- P35 **Novel bio-based copolyesters derived from ricinoleic acid**
A. Celli,¹ M.B. Banella,¹ C. Gioia,² P. Marchese,¹ M. Vannini,¹ M. Colonna,¹
¹Alma Mater Studiorum, University of Bologna, Department of Civil, Chemistry,
Environmental and Materials Engineering, Bologna, Italy; ²KTH Royal Institute of
Technology, School of Chemical Science and Engineering, Fibre and Polymer
Technology/WWSC - Division of Biocomposites, Stockholm, Sweden
- P36 **Application of specialty lipases in chemo-enzymatic processes**
Henrike Brundiek, Philipp Süss, Rainer Wardenga
Enzymicals AG, Greifswald, Germany
- P37 **Catalytic functionalisation of starch and amylose using plant oils:
towards polymeric materials and composites**
Philip B.V. Scholten,^{1,2} Zafer Söyler,¹ Christophe Detrembleur,² Michael A. R.
Meier¹
¹Institute of Organic Chemistry, Karlsruhe Institute of Technology, Karlsruhe,
Germany; ²Center for Education and Research on Macromolecules, Université
de Liège, Liège, Belgium
- P38 **Sustainable functionalization of bacterial cellulose for the design of
innovative bio-based nanomaterials**
G.Chantereau^{1,2}, ¹Department of Chemistry, University of Aveiro, Aveiro,
Portugal; ²Laboratoire de Chimie des Polymères Organiques, Pessac, France
- P39 **Life Integrated Process for the Enzymatic Splitting of triglycerides**
Detlef Klatt,³ Matthias Kraume,⁴ Sandrine Lacourt,¹ Rob Meier,⁵ Yann Raoul,¹
Aelig Robin²
¹Oleon NV, Belgium; ²Biocatalysts, United Kingdom; ³STC-Engineering GmbH,
Germany; ⁴Technical University Berlin, Germany; ⁵DSM, Netherlands
- P40 ***Hermetia illucens* L.: A Source for Crude Fat for Industrial Use**
Markus Hellmund, Peter Katz, Heinrich Katz, Hermetia Baruth GmbH,
Baruth/Mark, Germany

Abstracts

Part 1: Lectures

DENDROREFINING: SUSTAINABLE CHEMISTRY WITH WOOD BASED PRODUCTS

Markus Antonietti*, Max Braun, Davide Esposito, Valerio Molinari
Max Planck Institute of Colloids and Interfaces
Research Campus Golm, Potsdam, Germany
office.cc@mpikg.mpg.de

Hydrothermal reforming (HTR) and hydrothermal carbonization (HTC) are chemical processes to turn carbohydrates (including crude forestry side products, but waste biomass in general) into products which –depending on reaction conditions- can result in value chemicals but also artificial peat (for soil improvement) and industrial high value carbons.

All these processes occur naturally, but are highly accelerated under hydrothermal conditions. Lactid acid “fermentation” for instance can be ran from glucose with very high yields in only 3 minutes, without biocatalysts. Even coalification as the final product is highly accelerated to about 1 – 24 h reaction time by employing elevated temperatures between 180 – 230 °C and appropriate catalytic schemes. The processes not only work with a broad variety of “waste biomasses”, they are also exothermic and therefore potentially independent of outer energy sources.

In this talk, I will also present some new HTR processes and a variety of the potential products generated, such as lactid acid, valerolactone, dimethylfurane, but also new ionic liquids and ionic liquid polymers, bio-based methacrylate replacements, lignin-based phenols and products made thereof. I will also try to evaluate the potential and scale of such type of technologies

Recent Publications:

- 1) Hu, B; Wang, K; Wu, LH; Yu, SH; Antonietti, M; Titirici, MM: Engineering Carbon Materials from the Hydrothermal Carbonization Process of Biomass ; *ADVANCED MATERIALS* 22, 813-828, 2010
- 2) Titirici, MM; Antonietti, M: Chemistry and materials options of sustainable carbon materials made by hydrothermal carbonization; *CHEMICAL SOCIETY REVIEWS* 39, 103-116, 2010
- 3) Esposito, D; Kirchhecker, S; Antonietti, M : A Sustainable Route towards Imidazolium Building Blocks Based on Biomass Molecules ; *CHEMISTRY-A EUROPEAN JOURNAL* 19, 15097-15100, 2013
- 4) Esposito, D; Antonietti, M Chemical Conversion of Sugars to Lactic Acid by Alkaline Hydrothermal Processes *CHEMSUSCHEM* 6, 989-992, 2013
- 5) Esposito, Davide; Antonietti, Markus : Redefining biorefinery: the search for unconventional building blocks for materials *CHEMICAL SOCIETY REVIEWS* 44, 5821 – 5835, 2015
- 6) Molinari, Valerio; Clavel, Guylhaine; Graglia, Micaela; Antonietti, Markus: Mild Continuous Hydrogenolysis of Kraft Lignin over Titanium Nitride-Nickel Catalyst, *ACS CATALYSIS* 6, 1663-1670, 2016

L2

Next-generation block polymers from renewable feedstocks

Marc A. Hillmyer

Department of Chemistry & Center for Sustainable Polymers
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Sustainable block polymers hold much promise as tomorrow's advanced macromolecular materials. In this presentation I will describe our work aimed at the development of next-generation sustainable polymers that (i) can be produced from renewable resources on large scale, (ii) can be incorporated in block polymers with precision control over molar mass and composition, and (iii) exhibit properties that can outperform traditional petroleum derived materials from a combined environmental and mechanical property perspective. Key to the success of this strategy was the development of a biosynthetic pathway to a methyl-substituted valerolactone in collaboration with a team of metabolic engineers and its subsequent controlled incorporation in triblock polymers and polyurethanes in collaboration with a team of materials scientists. This comprehensive strategy offers an economically viable approach to both sustainable elastomers and plastics for a broad range of applications. I will describe background work that enabled this discovery, the initial efforts focused on beta methyl valerolactone, incorporation of this new biorenewable feedstock into chemically recyclable polyurethanes and highlights from a comprehensive study aimed at uncovering key design principles associated with the development of aliphatic polyester block polymers. I will end the presentation with new, related efforts coming from the Center for Sustainable Polymers (csp.umn.edu).

Biosynthesis and accumulation of lipids in novel bacterial isolates from the desert in Saudi Arabia

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Oleaginous microorganisms represent potentially an upcoming novel feedstock for the biotechnological production of lipids or lipid-derived biofuels. Because bacterial lipids are attracting more and more attention as sustainable replacement for mineral oil in fuel and also plastic production, we searched for novel, lipid-producing strains in desert soil. Accumulation of storage lipids as energy reserve and source of metabolic water represents a common adaptation in desert animals, which outlast long periods in the absence of drinking water by metabolizing their body fat. Desert bacteria could presumably follow similar mechanisms. Ten lipid-accumulating bacterial strains, affiliated to the genera *Bacillus*, *Cupriavidus*, *Nocardia*, *Rhodococcus* and *Streptomyces*, were isolated from arid desert soil due to their ability to synthesize poly(3-hydroxybutyrate), triacylglycerols or wax esters. Particularly two *Streptomyces* sp. strains and one *Rhodococcus* sp. strain accumulated significant amounts of TAG under storage conditions under optimized cultivation conditions. *Rhodococcus* sp. A27 and *Streptomyces* sp. G49 synthesized approx. 30% (w/w) fatty acids from fructose or cellobiose, respectively, while *Streptomyces* isolate G25 reached a cellular fatty acid content of nearly 50% (w/w) when cultivated with cellobiose. The stored triacylglycerols in the latter bacterium were composed of 30-40% branched fatty acids, such as anteiso-pentadecanoic or iso-hexadecanoic acid. To date, this represents by far the highest lipid content described for a member of the streptomycetes. A biotechnological production of such lipids using (hemi)cellulose-derived raw material could be used to obtain sustainable biodiesel with a high proportion of branched-chain fatty acids to improve its cold-flow properties and oxidative stability. A literature survey of single studies revealed that more than 50 % of the total community sizes in hot deserts appear to be favorable for lipid-accumulative species whereas it was lower in humid soil (≤ 20 %) and in cold deserts (≤ 17 %). Low bacterial lipid accumulation in cold deserts is assumed to result from the influence of low temperatures on fatty acids and the increased necessity of permanent adaptation methods.

L4

Catalysis for Introducing, Removing and Shuttling Functional Groups

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The development of efficient homogeneous catalytic reactions to transform widely available starting materials into value-added products is of critical importance to the molecular sciences. In this contribution, the design and discovery of new catalytic transformations of both renewable and petroleum-derived starting materials will be discussed. In particular, our recent progress in the development of inexpensive first-row transition metal catalysts for the synthesis of functionalized products through hydrocarbon amination,^{1,2} polyol deoxygenation³ and shuttle catalysis^{4,5,6} will be briefly discussed.

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L5

Intensifying homogeneous catalysed reactions with fatty compounds

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In the talk two cases of integrated process-developments for fatty compounds will be presented for the hydroformylation and hydroaminomethylation (HAM). These two homogeneous catalyzed reactions are able to convert oleo-chemicals to linear α,ω -functionalized molecules for e.g. biopolymers. Recovery of the valuable homogenous catalyst is one of the main tasks in order to develop an economical process.

In this context we developed a new recycling concept for the hydroformylation of methyl 10-undecenoate in laboratory scale batch experiments. The reaction system consisted of an aqueous phase containing the water soluble rhodium catalyst and 1-butanol containing the substrate allowing high reaction rates and good catalyst recovery in several recycling experiments. Furthermore, this knowledge was conducted to develop a continuous process in a miniplant scale.

A different atom-efficient tandem catalytic procedure under hydroformylation conditions (HAM) have been developed by us for the conversion of methyl 10-undecenoate. These linear products can be isolated from the reaction mixture by crystallization, and thus allow for their isolation in high purity, potentially polycondensation grade. The so synthesized linear diesters and diols are ready to show their performance in renewable polycondensates.

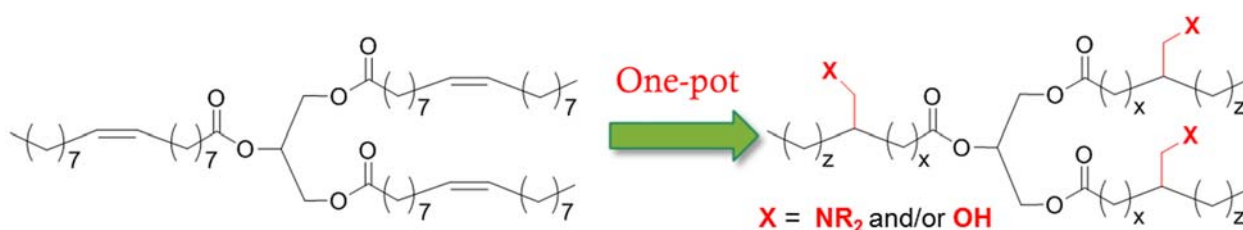
L6

One pot synthesis of hydroxylated or amino-hydroxylated triglycerides

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The direct functionalization of the carbon-carbon double bonds of triglycerides is of major interest to access biosourced building blocks with unique molecular and functional properties. In this study we described the synthesis of hydroxylated and amino-hydroxylated triglycerides. The reaction proceeds via a hydrohydroxymethylation reaction or a hydroaminomethylation/hydrohydroxymethylation sequence. Contrary to procedures described in the literature, no phosphane was used to coordinate the Rh-species, thus giving our strategy an industrial potential. Tertiary amines are used as ligands to promote the hydrohydroxymethylation reaction while secondary amines enable the hydroaminomethylation/hydrohydroxymethylation cascade reaction. The proportion of hydroxyl or amino groups grafted onto the triglyceride fatty chains was optimized by a careful choice of the experimental conditions, especially the nature and the amount of amine, the reaction temperature, and the CO/H₂ pressure. The resulting hydroxylated and amino-hydroxylated triglycerides are unprecedented biosourced building blocks, especially for polymer chemistry.



L7

A modified Wacker Oxidation process: efficient oxo-functionalization of fatty acid derivatives for the synthesis of renewable basic chemicals and polymers

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The utilization of fats and oils as renewable feedstock in polymer chemistry has become ever more important during the last decades, since these materials offer various application possibilities and a sustainable as well as an economically attractive alternative to depleting fossil resources.^[1] Moreover, the development of processes using catalytic amounts of transition metals and stoichiometric environmentally friendly oxidants, such as molecular oxygen, is a major goal in organic chemistry. Within this contribution, a modified Wacker Oxidation process was applied to achieve ketone-functionalization of unsaturated fatty acid methyl esters (e.g. methyl 10-undecenoate, methyl oleate) using a high pressure reactor system.^[2,3] For this purpose, catalytic amounts of palladium chloride were used in the presence of a dimethylacetamide/ water mixture and either molecular oxygen or synthetic air as re-oxidant. The obtained ketone FAMEs represent an interesting class of starting materials for further chemical modification *via* Baeyer-Villiger Oxidation, reduction or reductive amination, enabling the synthesis of various monomers (e.g. AB-type, dimer fatty acid methyl ester) and the thereof derived polymers.

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Photobiocatalytic Synthesis of Biogenic Olefines

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Decarboxylases are emerging as sustainable catalytic tools for C-C bond breaking under mild reaction conditions. A recently discovered bacterial decarboxylase (OleT) catalyses the conversion of fatty acids into terminal olefins in aqueous systems and at room temperature. OleT uses the peroxide shunt, in which hydrogen peroxide directly forms the catalytically active oxoferryl species that is required for breaking the C-C bond. In this study, we chose photocatalysis [2] as inexpensive and robust method for H₂O₂ generation. Using cell-free extracts containing a recombinant fatty acid decarboxylase, the photobiocatalytic system proved to be efficient for olefine synthesis. The photobiocatalytic decarboxylation proved to be an efficient catalytic system for the decarboxylation of ω -functionalized fatty acids with a high functional group tolerance.

The resulting α,ω -alkenols and α,ω -vinylcarboxylic acids are precursors for the synthesis of bio-based polymers. The talks discusses the combination of enzymatic catalyzed decarboxylation with other enzymatic and chemical transformations for the synthesis of bio-based antioxidants [3] and diols.

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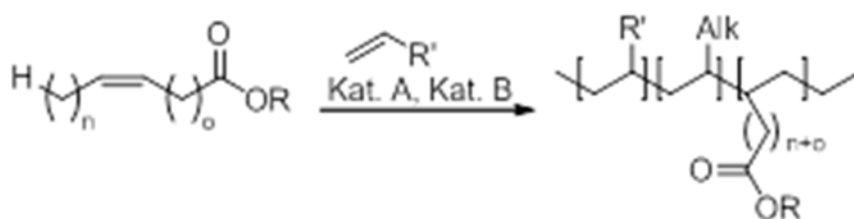
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First Direct Co-Polymerization of Internal Unsaturated Fatty Acid Esters with α -Olefins

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The direct utilization of natural, internal unsaturated fatty acids esters as monomers in the co-polymerization with unfunctionalized α -olefins was achieved for the first time. For this purpose, the co-polymerization reaction is combined one-pot with an in-situ isomerization of the internal double bond of the fatty acid ester, delivering the polymerizable, terminal olefin in a very low but replenishable amount. For the isomerization, e.g. $(\text{MeCN})_2\text{PdCl}_2$ is used, for the polymerization the Brookhart Pd(II) catalyst. The fatty acid ester does not need any particular pre-treatment. Methyl oleate as well as triglycerides like high oleic sunflower oil can be used under the conditions of the isomerizing co-polymerization. The obtained products are highly branched polymers with low glass transition temperatures. They have molecular weights up to 200 kDa and low polydispersity, indicating a living polymerization. The products are characterized by NMR, FTIR, and ESI-MS proving the incorporation of typically 5-10 weight-% of the functionalized, fat based monomer.



L10

Linear selective isomerization / hydroformylation for ω -functionalization of fatty acid methyl esters

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Fatty acids and their derivatives are a very interesting renewable feedstock for the chemical industry since they naturally contain a carboxyl function in combination with a long carbon chain. Consequently, they are widely applied as starting material, e.g. in surfactant synthesis. Additionally, unsaturated fatty acids can be converted into bifunctional molecules with interesting properties.

Especially the conversion of an unsaturated fatty compound into an α,ω -functionalized long chained molecule is of high interest for the synthesis of new bio based polymer precursors. Unfortunately, these reaction sequences are very challenging and place high demands on the applied catalysts. To reach high turnover frequencies, high yields and high selectivities a catalyst has to be extremely active in double bond isomerization, highly chemoselective for the desired functionalization and also highly regioselective towards functionalization in the terminal position. The fact, that internal double bonds are thermodynamically favored over terminal ones makes this task even more difficult.

From particular interest in this context are isomerization / carbonylation tandem reactions like alkoxy-carboxylations or hydroformylations since they enable the incorporation of the complete carbon chain of the fatty acid for the synthesis of potential polymer precursors.

While techniques like isomerizing methoxycarbonylation lead to symmetrical α,ω -functionalized molecules in high yields and with high selectivity, there is no efficient carbonylation reaction of unsaturated fatty acid methyl esters into asymmetrical α,ω -functionalized molecules.

A transformation with high potential for this kind of conversion is the isomerizing hydroformylation (Scheme 1). However, until now the highest yield of the α,ω -functionalized product of this reaction reported in literature is 26%.^[1]

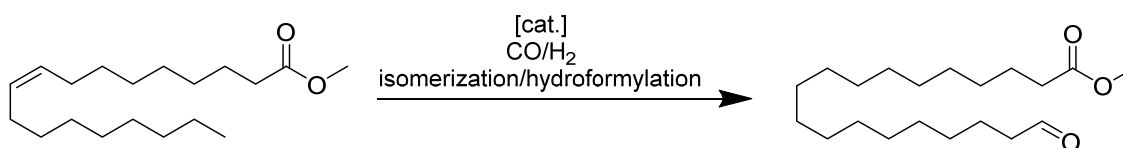


Figure 1: Isomerizing hydroformylation of methyl oleate.

Main problems in this conversion are the low *n*-selectivity in the hydroformylation and the high amounts of the hydrogenated substrate as byproduct. Consequently, development of a catalyst which does this transformation in an efficient manner would be of high value.

In order to overcome the limitations mentioned above, we decided to develop an orthogonal tandem reaction using two different catalysts: One catalyst for the isomerization, one catalyst for the *n*-selective hydroformylation of the terminal double bond. The methodical approach is shown in figure 2.

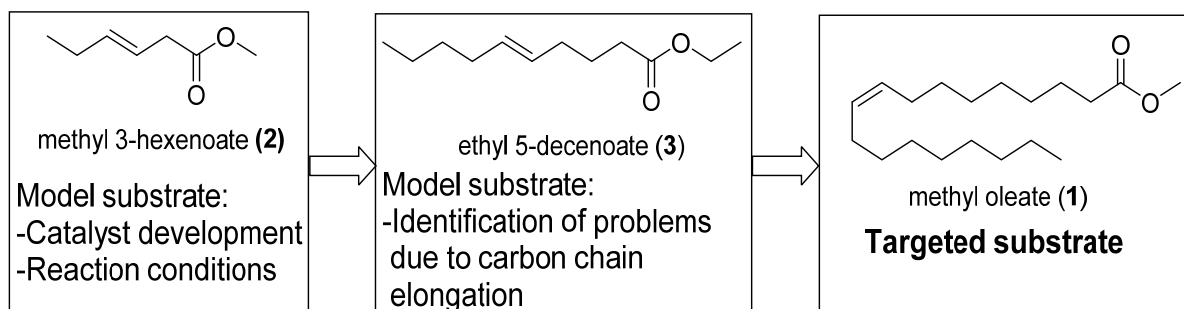


Figure 2: Methodical approach.

We started the development of the catalytic system using short chained methyl 3-hexenoate as model substrate. It turned out that a combination $\text{Rh}(\text{CO})_2\text{acac}/\text{biphephos}$ as hydroformylation catalyst and $\text{Pd}(\text{t-Bu}_3\text{P})_2/\text{PdI}_2$ lead to a high yield (81%) of the linear aldehyde and an excellent *n*-selectivity of 98%.

Afterwards, we used ethyl 4-decenoate as a second model substrate to identify problems occurring, if the carbon chain is elongated. Under optimized conditions the yield of the linear hydroformylation product was 75% and *n*-selectivity 95%. The last step was the application of the developed orthogonal tandem catalytic system for the conversion of the methyl oleate into the α,ω -unsymmetrical functionalized product (Scheme 1). Desired linear aldehyde was obtained with a yield of 67% and an excellent *n*-selectivity of 91%. To the best of our knowledge, these are the highest yields in the isomerizing hydroformylation of fatty acid methyl esters reported today.

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Properties of plant oil derived polyesters and thereof catalytically obtained polyethers

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Oils and fats stand out as one of the most important renewable resources for the synthesis of monomers and polymers. Recently, we have reported a novel reaction protocol allowing the reduction of methyl oleate^[1] and high oleic sunflower oil^[2] to the respective ethers. While the reducing agent 1,1,3,3-tetramethyldisiloxane (TMDS) is used in stoichiometric amounts, GaBr₃ can be used in catalytic amounts of 0.5-1 mol%. The reaction is carried out under mild conditions giving full conversion of the substrate. Here, this protocol is introduced as novel method to obtain new polyethers, which would produce high amount of waste when applying classic synthesis approaches (i.e. ether synthesis by nucleophilic substitution). Using mostly plant oil derived carboxylic acid esters as starting material, two different routes are pursued: In the first route, plant oil derived polyesters are synthesized and afterwards reduced to the corresponding polyethers. Moreover, a systematic study of the reduction of polyesters with different structures between the ester linkages is performed to explore possible limitations. In the second route, α,ω -unsaturated ester monomers are synthesized from fatty acid methyl esters, reduced and polymerized afterwards. The combination of self-metathesis, ethenolysis and ADMET polymerization as synthetic methodologies enables the production of the polyethers in a sustainable fashion.

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Synthesis of chemicals from renewable feedstocks catalysed by heteropoly acids

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Heteropoly acids (HPAs), comprising nanosized oxometal cluster polyanions, have attracted much interest in catalysis, both in academic research and industrial applications, offering significant economic and environmental benefits. The aim of this presentation is to discuss recent results of the author's group on the use of catalysis by HPAs for the synthesis of chemicals from renewable feedstocks focussing on reactions of terpenes and glycerol.

Terpenes, found in essential oils of plants, represent sustainable and versatile feedstock for the synthesis of flavours, fragrances and medicines (e.g., alpha- and beta-pinene, 350,000 t/y). Acid catalysis plays a key role in terpene chemistry. Traditionally, mineral acids (e.g., H₂SO₄) are used as catalysts in large, over-stoichiometric quantities, with adverse impact on the environment. Therefore, the development of new acid catalysts for cleaner processing is a challenge. It is demonstrated that HPAs are efficient and environmentally friendly catalysts for acid-catalysed terpene reactions such as hydration, esterification, etherification, cyclization and isomerization in homogeneous and heterogeneous systems. These reactions can provide clean routes to valuable ingredients and intermediates for the fragrance and pharmaceutical industries.

The growing worldwide production of biodiesel has made a large amount of glycerol available as a renewable feedstock for the synthesis of chemicals. Dehydration of glycerol to acrolein is one of the most important directions for the utilisation of glycerol. HPAs are very efficient catalysts for this reaction in the gas phase. Other discussed examples include hydrogenolysis of glycerol to propanediol using bifunctional catalysts comprising HPAs doped with platinum group metals.

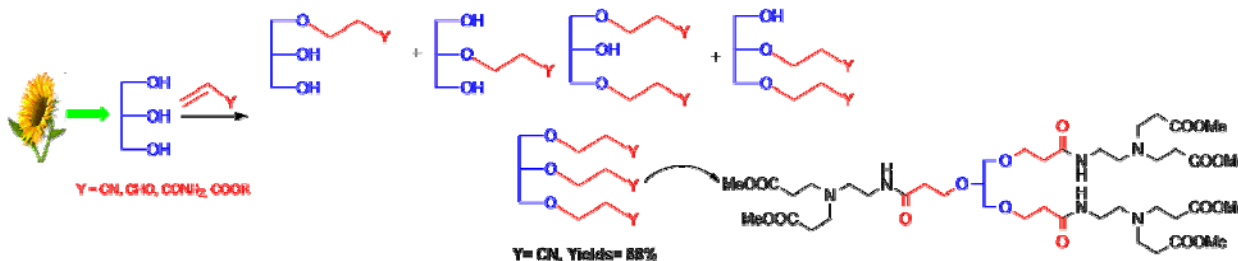
L13

A new core of dendrimers from glycerol by nucleophilic addition of glycerol to acrylic compounds

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Glycerol is a common building block in organic chemistry¹ and new derivatives or applications have been developed. The etherification of glycerol, generally realized under heterogeneous acid catalysts² or by reductive alkylation³, leads functionalized products. In contrast, Michael addition of glycerol to acrylic compounds was less studied. To our knowledge, the cyanoethylation of glycerol was first described by Bruson⁴ and more recently, Trinadh et al. obtained the tri-(2-cyanoethyl)glyceryl ether with 8% yield using Amberlyst A-21 polymer resin⁵.

In this communication, we investigate the etherification reaction by nucleophilic addition of glycerol to acrylic compounds in basic conditions. The reactivity of acrylic compounds was studied in presence of catalysts and without organic solvent.



Tricyanoethylglycerol was obtained in 88% (purity 99%) without purification methods. The tricyanoethylglycerol was used as a new prochiral core for the synthesis of poly(amidoamine) dendrimer⁶.

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Oligomerization of glycerol carbonate esters

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The ring-opening oligomerization of the 5-membered cyclic carbonates is carried out with a thermodynamic difficulty and a substantial partial loss of carbonate units of at least 50% [1,2]. On the one hand, the five-member ring opening enthalpy is positive and represents a thermodynamic energy barrier to overcome. On the other hand, the polymerization of cyclic carbonates by opening the five-membered ring is promoted by organometallic catalysts, metal catalysts and organic catalysts.

Our study focuses on the oligomerization of short and medium-chain glycerol carbonate esters (ECGs) from C2 to C11^[3,4,5,6,7], by ring opening assisted by glycerol to overcome the thermodynamic barrier. Thus, an experimental design was carried out using a 8.5 L home-made reactor making it possible to control the self-generated high pressure, the reaction temperature (thermodynamic) while studying the reaction time and the amount of organic-metal catalyst (kinetic), parameters to be controlled in order to open the 5-membered carbonate ring of the ECGs. Thus, the operating conditions were optimized as a function of the ECG conversion, the composition of the oligomerization reaction medium, the content in carbonate functions and as a function of the type or family of oligomers. For this purpose an analytical matrix has been set up to allow the crossing of analytical data: HPLC giving access to quantitative composition data and sample collection, ¹H NMR, ¹³C quantitative and Maldi-tof mass spectrometry giving access to the structural characterization of the oligomers. Thus, a new way of opening the 5-membered carbonate rings has been developed giving mixtures of interest for industrial applications [8,9].

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Next Generation Sugar-based Vegetable Oil Structuring Agents: Synthesis, Assembly, Morphological Evaluation and Applications

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The use of vegetable oils, instead of solid fats, has been receiving special attention due to their nutritional and health benefits associated with unsaturated fatty acids (UFAs). However, efforts to incorporate the oils in food products are challenged by lack of similar organoleptic properties and oxidative stability as those of fat-structured food materials; the oils are prone to oxidation due to the presence of UFAs. The techniques adapted to solve these issues include partial hydrogenation and addition of solid fat and synthetic antioxidants. However, the limitations include, for instance, catalytic hydrogenation leads to *trans fats*, which are being restricted use owing to growing health concerns. To address the current challenge, multifunctional low molecular weight gelators (LMWGs) are proposed to impart both mechanical and oxidative stability to oils. Selecting optimal precursors from plant sources and combining the capabilities of biocatalysis in a GRAS protocol, we have successfully designed and demonstrated an array of simple sugar alcohols (mannitol, sorbitol, xylitol and erythritol), glucoside (raspberry ketone glucoside) and disaccharide (trehalose) based LMWGs as multifunctional structuring agents, exploiting their low-/non-caloric and antioxidant properties. Structuring ability was systematically tested in edible oils such as canola, soybean, olive and corn oils, which created excellent oil gels (*oleogels*) with minimal gelator concentration. The nature and aesthetic value (transparency/opaqueness) of the *oleogels* can be tuned by gelator concentration, nature of oil, etc. The study also aims at finding the correlation between textural and organoleptic properties against the nanostructure and rheology of the *oleogels* for future food applications.

Oleochemical carbonates from CO₂ and renewables

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The chemical fixation of CO₂ into valuable products has attracted much attention in recent years. In this context the conversion of CO₂ with epoxides to the corresponding cyclic carbonates is an attractive and extensively studied reaction. We are generally interested in the synthesis of cyclic carbonates from petrochemical as well as renewable feedstocks. Recently we reported efficient sustainable metal-based^[1] two component catalyst systems enabling the conversion of CO₂ with epoxides under mild conditions. Subsequently a structural design concept for one-component organocatalysts for this reaction was proposed which proved to be viable.^[2] Furthermore, we evaluated different concepts for the recycling of these catalyst, e.g. by immobilization and organic solvent nanofiltration.^[3]

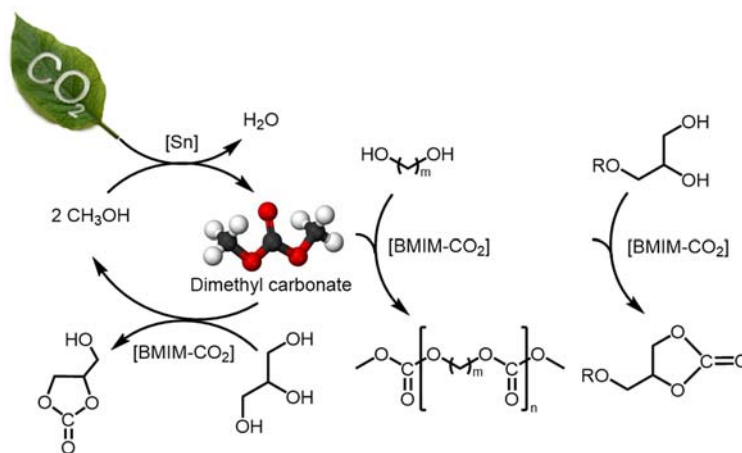
Most recently we turned our attention to the atom-economic reaction of CO₂ and epoxidized oleochemicals.^[4] Notably, these products are obtained in yields up to 99% from CO₂ and renewable feedstocks under comparatively mild and solvent-free reaction conditions. Furthermore, in respect to carbon they are based on >99% CO₂, combining biological and chemical CO₂ and thus represent an excellent example for Green Chemistry. We will discuss our efforts in cyclic carbonate synthesis with the emphasis on oleochemical carbonates.

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Catalytic Transesterification of Organic Carbonates with Bio-based Building Blocks

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Our group has been working for a long time in the field of organic carbonates, focusing in particular on the direct synthesis of linear alkyl carbonates from carbon dioxide and alcohols [1]. One of the target molecules is dimethyl carbonate (DMC). In parallel, transesterification reactions involving organic carbonates were also studied. In 2009 we reported an improved and greener approach for the synthesis of glycerol carbonate from glycerol and DMC. The zwitterionic species, 1-*n*-butyl-3-methylimidazoilium-2-carboxylate (BMIM-CO₂) was efficiently used as an organo-catalyst [2]. Since then, this approach has been extended to the field of polymers leading to the synthesis of aliphatic [3] and telechelic [4] polycarbonates. More recently we converted an undecylinic acid-based monoglyceride into a cyclic carbonate derivative which then reacts in the presence of diamines to afford polyhydroxyurethanes [5]. All these transesterification reactions will be detailed and discussed in the presentation.



The authors are grateful for financial supports from the Centre National de la Recherche Scientifique and the University of Bourgogne Franche-Comté.

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Synthesis and properties of new cross-linked bio-based aliphatic polycarbonates

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Presently, most of the industrial chemicals are produced from oil resources. However, rapid depletion and price increase of fossil resources are encouraging chemists to point their research towards designing chemicals and materials from renewable feedstocks. Fatty acid derivatives (FAD) appear as a versatile platform to develop bio-based polymers. Based on FAD, a lot of work has been done so far in the field of polyurethanes, polyesters, polyamides, etc. However, not as much attention has been paid to the preparation of aliphatic polycarbonates.

Aliphatic polycarbonates are used in widespread biomedical applications, due to their high biocompatibility, biodegradability, low toxicity, and better mechanical properties as compared to similar polyesters. Ring-opening polymerization of cyclic carbonates raised lot of attentions for the formation of aliphatic polycarbonates.

To that purpose, this presentation will discuss the synthesis of a large platform of fatty acid-based six-membered cyclic carbonates and their organo-catalyzed polymerization, leading to original functional linear aliphatic polycarbonates. Polycarbonate networks were also prepared that exhibit good thermo-mechanical properties and, in certain instances, were thermally reversible.

Life cycle assessment of bio-based, waterborne PU Adhesives for fast industrial bonding processes

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Aqueous PU dispersion adhesives based on high molecular weight, semi-crystalline polyurethane polymers have long demonstrated their outstanding performance and are a well-established bonding technology in several industrial applications. Due to their thermal activation properties and sharp melting area, these adhesives allow for efficient bonding processes with short bond strength build-up times. State-of-the-art is the use of polyester building blocks from fossil raw material resources to synthesize the base polymers.

As the use of biobased raw materials and sustainability is increasingly a factor in public and customer perception, it is also becoming increasingly important in industrial processes and company strategies. For these reasons, a consortium of industrial and research partners is working to develop bio-based solutions for PU dispersion adhesives using significant amounts (> 50 %) of renewable raw materials. Target applications include the automobile, furniture and shoe industries.

In order to investigate the environmental performance of the new biobased adhesive, a life cycle assessment is carried out. First results indicate that the carbon footprint of the adhesive can be reduced by more than 25% when comparing the biobased adhesive to fossil-based PU dispersions.

This project is supported by the “Fachagentur Nachwachsende Rohstoffe” (FNR) on behalf of the German Federal Ministry of Food and Agriculture (BMEL) by decision of the German Bundestag.

Non-Isocyanate route to Fatty acid-based polyurethanes: bulk and water-borne processes

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Thermoplastic poly(hydroxyurethane)s (PHUs) raised industrial and academic research interest, since their synthesis is achieved via the ring-opening of bis-cyclic carbonates with diamines, enabling the replacement of phosgene and isocyanates employed in the classical polyurethane (PU) manufacture. [1] In view of the fossil fuel depletion, the use of building blocks from renewable resources such as vegetable oils is on the rise. Combining PHUs synthesis and bio-based compounds, a large platform of fatty acid-based cyclic carbonates as poly(hydroxyurethane) precursors was synthesized by epoxidation/carbonation routes. However, such monomers exhibited a slow polymerization rate towards amines, due to the electron-releasing alkyl chains, which deactivate the cyclic carbonates. [2]

An alternative route consists in inserting a heteroatom nearby the cyclic carbonate to improve/activate its reactivity. Herein, the synthesis of new activated lipidic cyclic carbonates from glycerol carbonate and epichlorohydrin has been achieved, leading respectively to an ester or an ether linkage in β position of the carbonate. After kinetic investigations of the cyclic carbonate aminolysis on model compounds, the corresponding activated bis-cyclic carbonates were polymerized with various diamines and exhibited enhanced reactivities. A specific focus on the side reactions that could occur in both model reaction and polymerization will be discussed in this presentation. [3]

In addition, aqueous dispersions of PHUs by mini-emulsion polymerization were performed. This process was already described to prepare water-borne PUs dispersions, and, more recently, bio-based PUs, following the classical reaction of diisocyanates with diols. In this work, we specifically extended the miniemulsion polymerization process to the polyaddition of hydrophobe fatty acid-based bis-cyclic carbonates and diamines. [4]

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Latex-Based Pressure Sensitive Adhesives using Conjugated Linoleic Acid

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Free-radical emulsion terpolymerizations of conjugated linoleic acid/styrene/*n*-butyl acrylate (CLA/Sty/BA) were performed for the production of pressure-sensitive adhesives (PSAs) with significant renewable monomer content (>30 wt.%). Because of the ability of conjugated oils to copolymerize, CLA was chosen for free radical polymerization. With the prohibitive cost of high purity CLA an affordable CLA containing oleic acid and saturated fatty acids was used.

The emulsion terpolymers were characterized for composition, conversion, molecular weight and glass transition temperature while latexes were characterized for viscosity, particle size and both adhesive and mechanical properties. The oleic acid impurity found in the lower cost CLA was shown to influence the reaction kinetics significantly. Adhesive performance was tuned using divinylbenzene (DVB) crosslinker to keep the terpolymer molecular weight in a desired range. By using a constrained mixture design, the influence of terpolymer composition, chain transfer agent (CTA) concentration, DVB concentration, molecular weight, viscosity and particle size on tack, peel strength and shear strength was investigated. Our objective to incorporate significant amounts of a renewable monomer, CLA, into a latex-based adhesive formulation was achieved with 30 wt.% incorporation.

Optimization studies on viscosity and thermomechanical properties of highly methacrylated bio-based resins

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Bio-based thermosets have previously been produced from free-radical curing of methacrylated epoxidized sucrose soyate (MESS) [1]. These thermosets have shown high glass transition temperature (T_g) and good mechanical properties, but the resin viscosity was high. This issue was circumvented by further functionalization of the MESS to dual methacrylated epoxidized sucrose soyate (DMESS). The structure-property relationships of the thermosets produced were studied. Nevertheless, the thermosets produced from DMESS remained brittle. To maintain low viscosity and improve ductility, replacement of some methacrylate groups with various ester groups was hypothesized. The synthesis of these modified DMESS remained as a one-pot process involving the sequential slow addition of anhydrides mixed prior to addition.

The resins were characterized using Fourier transform infrared spectroscopy (FTIR), proton nuclear magnetic resonance spectroscopy ($^1\text{H-NMR}$), gel permeation chromatography (GPC), and viscosity measurements. Formulations were made using varying amounts of styrene and free-radically cured using commercially available peroxyesters as initiators. The extent of cure was determined by gel content using Soxhlet extraction and confirmed using FTIR. The thermal and mechanical properties were evaluated using thermogravimetric analysis (TGA), dynamic mechanical thermal analysis (DMTA), and tensile testing.

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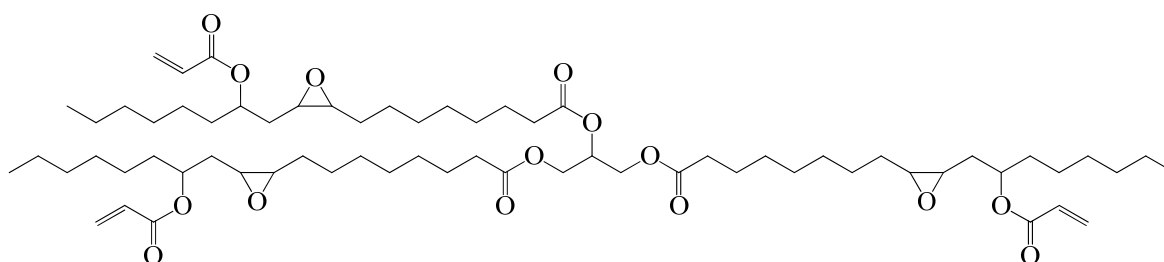
New Type Biobased Difunctional Monomers: Epoxidized Acrylated Derivatives of Castor Oil

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Plant oil triglycerides are versatile compounds. They are readily available and contain reactive parts. Unfortunately the polymers of plant oil triglycerides show poor mechanical and thermal properties when they compared with petroleum based counterparts. The synthesis of new type plant oil based monomers that they give polymers which exhibit improved mechanical and thermal properties is desired. Most of the plant oil triglycerides are classified simple triglycerides and they are the esters of saturated or unsaturated fatty acids. Besides these simple triglycerides some natural plant oils are inherently contains functional groups. Castor oil is the one of the most abundant functional plant oil. Castor oil is the ester of glycerol and ricinoleic acid. New type of epoxy acrylates of castor oil and castor oil derivatives are synthesized in two step. Acrylation of castor oil or its derivative is performed in the first step and the epoxidation via Prilezhaev reaction is completed in the second step. The monomers of epoxidized and acrylated derivatives of castor oil shows low viscosity and the polymers showed improved mechanical and thermal properties. In the figure one of the epoxy acrylate derivative of castor oil is shown.



Epoxidized Acrylated Castor Oil
(EACO)

L24

Diels-Alder and cationic polymerization of monomers derived from plant oils and furans

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This lecture will discuss, on the one hand, the application of the furan/maleimide thermally reversible Diels-Alder reaction to the synthesis of novel macromolecular materials based on plant-oil-derived monomers and the properties of the ensuing polymers. On the other hand, ongoing studies will be reported on the cationic polymerization of tung oil and its fatty acid, as well as their copolymerization with furfuryl alcohol.

Unfold Innovation with original lipidic hyperbranched polyesters

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New bio-based hyperbranched polyesters (HBPE), patented in 2015, were synthesized in the framework of the precompetitive research program GENESYS of the SAS PIVERT in partnership with ITERG (French Institute of oils and fats) and LCPO (University of Bordeaux).^{1,2}

Hyperbranched polymers, traditionally petroleum-based, are characterized by a branched structure whose density is flexible and by a high level of functional groups. Due to their particular properties (lower viscosity than dendrimers, higher functionality, better solubilities), these macromolecules are used as additives or materials for encapsulation in many fields.

Hence, our sunflower, rapeseed or castor seeds-based hyperbranched polyesters could have a wide range of applications: encapsulation of actives, rheology modifiers or even additives to modify mechanical properties of various formulations (adhesives, cosmetics, paints, etc). In addition, the post-functionalization of the large number of peripheral hydroxyl functions could be envisaged to introduce hydrophilicity for the cosmetic industry.

Now, the SAS PIVERT is producing samples of original bio-based hyperbranched polyesters, evaluating their applications, targeting markets and realizing a techno-economic analysis. Partners wishing to mature or license the technology are also seeking ou

¹ „New branched polymers, their preparation process, and uses thereof” Patent application WO 2016/059230 A1.

² “Polyesters par couplage thiolène ” Patent application FR 15 60389.

Structure property relationship of lignin inspired phenolic polyethers synthesized via ADMET

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In the past years, there has been a strong development in the field of polymer synthesis from renewable monomers, to provide alternatives to or replacements for crude oil based monomers. Some polymers based on renewables are already available on an industrial level. Yet, these polymers are largely derived from carbohydrates or triglycerides as renewable resources. However, a significant share of industrially relevant polymers contains aromatic entities to ensure certain thermal and mechanical properties. Nowadays, renewable aromatic compounds can be derived from cashew nutshell liquid, polyphenols and lignin.¹ Lignocellulosic biomass is an especially promising resource since it is abundant and does not compete with food or feed.

Key intermediates in the synthesis of renewable aromatic building blocks from lignin are vanillin, 4-hydroxybenzaldehyde, and syringaldehyde, which can be converted into diols.³ A platform, consisting of dienes, was synthesized from potentially renewable lignin-derived diols containing an aromatic moiety and other renewable diols with a related structure (14 diols in total). Subsequently, ADMET polymerization was performed on this series of dienes in order to investigate the influence of the aromatic substitution pattern in the monomers on the resulting thermal properties of the polymers. In addition, the remaining double bonds of the polymers, synthesized by ADMET polymerization, allow for further fine-tuning of the material properties by post-polymerization functionalization or crosslinking via triazolinedione chemistry.²

³ Caillol, S., *et al.* Green Chemistry. 2014;16(4):1987-1998.

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Unconventional renewable raw materials as sources for lubricants

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Since the nineties of the last century the material and energetic use of renewable raw materials gets promoted in an increasing range by politics, science and economy, as the hitherto nearly solely used fossil resources have to be regarded critically due to their negative contribution to the climatic development. The continuous increase of the usage of renewable raw materials gets supported by standardising measures and specific research projects, enabling the use of new sources of renewable raw materials, which could not be used in the background. Bio lubricants are one important product group and are requested to contain preferably high amounts of renewable raw materials. This offers the potential of economic and ecological advantages, as bio-based lubricants, in comparison to fossil based lubricants, mostly possess lower toxicities and better biodegradability. Additionally the substitution of fossil materials can affect the eco balance in a positive way, as renewable raw materials possess a closed cycle of matter.

A promising approach for the development of biogenic lubricant components would be the application of photosynthetic micro algae, as algae can possess an up to approx. ten time's higher biomass crop in comparison to rooted plants (in relation to the area under cultivation). The algae biomass contains a technically relevant lipid fraction of approx. 20% in the form of triglycerides. This fraction can be extracted from the biomass and be carried to a substantial use as lubricant or lubricant component respectively.

Another usable source for renewable raw materials are press cakes of rape seed. After exploitation of edible rape seed oil approx. 4 million tons of this material incurs per year in Germany. The press cake is only limited suitable for animal feed, as it often contains ingredients like e.g. glucosinolates and thus gets used energetically. However the press cake can contain a rest content of proteins up to approx. 40%, which could be made accessible to a technical utilization. For this purpose the proteins have to be extracted from the cake and can be modified e.g. by hydrolysis or chemical functionalization to enable technical applications.

Biocatalytic Cascades for the Synthesis of Alkenes, Dienes and Amino Acids from Fatty Acids

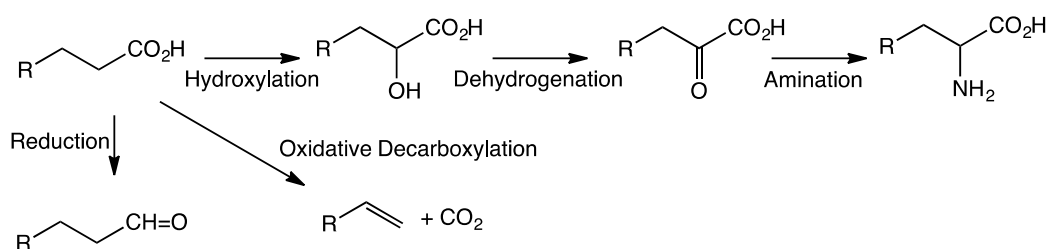
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Among the various classes of renewable carbon sources, fatty acids constitute a relatively homogeneous group of potential starting materials for organic synthesis. Aiming to exploit the chemo-, regio- and stereoselectivity of biocatalysts for the valorization of fatty acids, the following cascade-reactions were designed:

— Bioreduction of substituted mono- and dicarboxylic acids at the expense of ATP and NADPH using carboxylate reductases furnished the corresponding (mono)aldehydes in a stereoselective fashion.^[1]

— Oxidative decarboxylation of mono- and dicarboxylic acids using the monooxygenase P450 OleT gave the corresponding terminal alkenes and dienes, resp.^[2]

— α -Functionalization of fatty acids via enzymatic hydroxylation, followed by dehydrogenation of the corresponding α -hydroxy acids gave α -keto-acids as versatile intermediates. The latter could be aminated to yield L- α -amino acids in a cascade-like one-pot process with internal recycling of NAD(P)H and H₂O₂, respectively.^[3]



Acknowledgements: Funding by the Austrian BMWF, BMVIT, SFG, Standortagentur Tirol, Government of Lower Austria and ZIT through the Austrian FFG-COMET-Funding Program is gratefully acknowledged.

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Oils and CO₂, a promising combination for designing insulating foams and high performance coatings

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Making plastics more sustainable by valorizing waste CO₂ as a cheap, inexhaustible and renewable feedstock is an early stage technology with strong innovation potential that imposes itself as a strategic driver for developing future low carbon footprint materials and technologies. With a global production estimated to 18 million tons for 2016, polyurethane (PU) is one of the most important polymers in our everyday life applications (automotive, building and construction, coatings, etc.). Industrially, PU is produced by step-growth polymerization between di- or polyisocyanates and di- or polyols. However, isocyanates are toxic and drastic changes in the REACH regulations limiting/banning the use of isocyanates are expected. There is a need today to develop new greener and safer alternatives to produce PU. Valorizing CO₂ as C1 feedstock for producing precursors entering in the synthesis of polyurethanes by a non-isocyanate route (NIPU) is a promising strategy to solve this challenge.

In this talk, we will focus on the synthesis and characterization of novel NIPUs foams for thermal insulation, and NIPUs coatings for metal protection. Our research highlights benefit of merging bio-resources (such as vegetable oils) with carbon dioxide transformation.

In the first part of this talk, we will report on the fast synthesis of bio- and CO₂-sourced cyclic carbonates by coupling CO₂ with epoxides using a new highly efficient bicomponent homogeneous organocatalyst under solvent-free and mild experimental conditions. The mechanism of the activation of the reaction will be discussed, and scaling up of the technology will be demonstrated (15kg scale). In the second part, we will illustrate the use of these bio- and CO₂-sourced cyclic carbonates for the production of microcellular NIPU foams with closed cells morphology for thermal insulating applications, but also for preparing hybrid NIPUs coatings for metal protection.

New high-value chemicals, polymers and materials from renewable resources: a contribution to the development of the biorefinery concept

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In the last two decades there has been an increasing interest in the development of renewable alternatives to fulfill society needs of chemicals, polymers and materials, tackling the inevitable dwindling of fossil resources and the environmental problems associated with their massive consumption. The biorefinery concept, addressing the integrated and rational exploitation of biomass to achieve this goal is therefore a transdisciplinary field of research that has grown enormously in the last decades.

Given our previous experience in the agro-forest biomass chemistry and processing, in the last decade our group has been intensively working in several domains of this global challenge, notably in the extraction and upgrading of high-value components from biomass, in the production of biobased polymeric materials, and functional (nano)materials, with an overarching search for eco-friendly and sustainable processes.

Examples of extraction and upgrading of biomass components include the extraction of triperpenic acids from eucalyptus and oak cork, and the development of new methods for suberin extraction and valorization.

The production of poly(ethylene furandicarboxylate) and related polyesters- renewable analogs to the fossil based terephthalic acid counterparts, is among the most promising activities in the polymer chemistry domains.

Finally we have been intensively working in the development of (nano)cellulose based functional composites with a wide panoply of natural and synthetic polymers, with applications spanning from biomedical domains to proton exchange fuel cells, passing through films for transparent electronics.

A general overview of the research activities of the group with some cutting edge examples will be put forward during this presentation.

Abstracts

Part 2: Posters

Transesterification of wild chestnut oil

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Lipid fractions extracted from by-products possessing renewable active principles represent a real option for the diversification of the raw material basis for the most various fields. Their transesterification is a sustainable variant of valorization, which also meets the “green chemistry” desiderata. The serial process of three successive and reversible reactions [1] is decisively influenced mainly by the nature and accessed amount of the acid catalyst, the alcohol/lipid fraction molar ratio, the temperature and the amount of water present in the vegetable oil. The field literature specifies a wide variety of lipid fractions obtained from seed materials recovered from food, cosmetics and/or pharmaceutical processing. This work presents the major results of obtaining the oil from the fruit of wild chestnut (*Castanea vesca*), commonly found in the Western Plain of Romania, by repeated solid/liquid extractions [2], followed by the transesterification itself of the resulting lipid fraction with lower alcohols C₁-C₃. Its preliminary gas-chromatographic evaluation confirmed the presence of 10.4% C₁₆ (0Δ), 57% C₁₈ (1Δ), 28.8% C₁₈ (2Δ), and 3.7% C₁₈ (3Δ). The influence of the abovementioned factors was followed, favorable results being obtained for molar ratios lower alcohols C₁-C₃/lipid fraction between 15-30%; transesterification time 40 hours (60°C) for methanolysis, 20 hours (80-85°C) for ethanolysis, and 4 hours (reflux) for propanolysis, respectively. The acid catalyst added in a proportion of 1 mole %, dodecylbenzenesulfonic acid, favored, including by micellar catalysis, the obtention of practically quantitative yields. The alkyl esters obtained, purified by repeated liquid/liquid extractions, were characterized chemically and physico-chemically (acid number, ester number, iodine number, thin-layer chromatography). The product obtained will also be further evaluated by specific combustion indicators.

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Vegetable waxes with directed hydrophilicity/hydrophobicity

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Classical waxes, defined as esters of higher monocarboxylic acids with higher monohydroxy primary alcohols with straight chain and even number of carbon atoms, are complex mixtures. Vegetable waxes are foliar and/or fruit exudates (e.g., plum) with protective role in plant physiology. The supply and demand balance in the current market for these products is detrimental to the supply. Lipid fractions from vegetable (seed) by-products containing higher acids represent a real option for expanding the raw material basis necessary for balancing the referred balance. 2-Ethylhexyl alcohol is the partially branched higher alcohol at the lower end of the homologous series. It is a product of petrochemical processing ("oxo" synthesis) in the synthesis of higher (2-ethylhexyl) polyethoxylated alcohols with "homogeneous" ($n = 3-18$) oligomerization degrees (strictly directed). As a monohydroxy fraction after the esterification with abovementioned higher acids, it allows the diversification of the range of vegetable waxes with new competences. In this work, their synthesis is carried out in the following steps: (a) obtention and characterization of lipid fractions (higher acids) from dog-rose hips (*Rosa canina*). The preliminary gas-chromatographic evaluation of higher acids in dog-rose hip oil, widely spread in the spontaneous flora of the Western Plain of Romania, confirmed the presence of 3.19% C_{16} (0 Δ), 15.92% C_{18} (1 Δ), 67.50% C_{18} (2 Δ), and 13.30% C_{18} (3 Δ), respectively; (b) obtention and preliminary characterization of the "homogeneous" polyoxyethylene chain ($n = 3-18$) by directed Williamson synthesis [1]; (c) obtention and characterization of "homogeneously" ($n = 3-18$) polyethoxylated higher (2-ethylhexyl) alcohols; (d) obtention and actual characterization of the assortment of vegetable waxes with directed hydrophilicity/hydrophobicity. The dependence of synthetic yields was followed over various stages using classic indicators (hydroxyl number, acid number, iodine number, ester number, ethylene oxide content, etc.) and instrumental analysis (thin-layer chromatography, gas chromatography, infrared spectroscopy, etc.), respectively. Vegetable waxes with directed hydrophilicity/hydrophobicity meet the "green chemistry" principles and the latest EU directives regarding the toxicity and availability of the raw materials basis and work protocols.

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Graphene Based Heterogeneous Acid Catalysts for the Production of Biodiesel from Waste Cooking Oil

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The ever increasing demand of the renewable and sustainable energy sources in the modern world offers a challenge to develop the efficient catalyst and the catalytic processes. Conversion of vegetable oils into biodiesel by esterification is an upcoming technology for achieving green and sustainable energy. However acid catalysts are required to promote the esterification. Graphene has recently emerged as a catalyst support owing to its high surface area combined with other interesting properties. In our present study oxides of transition metals like Fe, Co, Ni, Cu and Zn supported on sulfonated graphene oxides were synthesized. Supporting non-noble metal oxides on graphene oxide was done according to the procedure reported in the literature. Sulfonation was carried out by treating with sulfuric acid. These catalysts were characterized by a variety of techniques, like Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), transmission electron microscopy (TEM), energy dispersive spectroscopy (EDS), atomic force microscopy (AFM), Raman spectroscopy, and thermo gravimetric analysis (TGA). Their catalytic activities were tested in the esterification of oleic acid with ethanol, at a molar ratio of alcohol to oleic acid of 12:1 with 5 wt% of catalyst at 100°C with a reaction time of 4h. Our study showed that magnetic materials like Fe, Ni, Co oxide supported sulfonated graphene oxide show conversion above 90%. Nanocomposite of Iron oxide - sulfonated graphene oxide (Fe₂O₃/GO-SO₃H) was the best catalyst, yielding 99% conversion of oleic acid to ethyl oleate. Further we used this catalyst to convert waste cooking oil (WCO) to biodiesel. We could achieve 78% of conversion using ethyl alcohol at temp 90°C. The fatty acid ethyl esters (FAEE) were characterized by proton NMR and GC-MS. Further we have developed acidified calcinated native clay from the lower Himalayas as a catalyst for the esterification of oleic acid. Characterization of this catalyst was done by XRF, XRD, BET, TGA etc. Further work is carried out using this catalyst for the transesterification of WCO.

Synthesis of Furyl-Containing Bisphenol Based on Chemicals Derived from Lignocellulose and its Utilization for Preparation of Clickable (Co) Poly(arylene ether sulfone)s

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Lignocellulose-derived chemicals such as furfural, syringol, guaiacol, etc are highly attractive as sustainable alternatives to petrochemicals for the synthesis of monomers and have attracted great attention of polymer community. We wish to report herein the facile synthesis of fully bio-based bisphenol containing pendant furyl group by base-catalyzed condensation of furfural with guaiacol-both of which are derived from lignocellulose. Bisphenol possessing pendant furyl group represent valuable monomer for the synthesis of a range of polymers which include epoxy resins, polyesters, polycarbonates, poly (aryl ether)s, etc. New (co) poly(arylene ether sulfone)s were prepared by polycondensation of 4,4'-(furan-2-ylmethylene)bis(2-methoxyphenol) or a mixture of 4,4'-(furan-2-ylmethylene)bis(2-methoxyphenol) and 4,4-(isopropylidenediphenol with 4,4'-(fluorodiphenyl sulfone) in N N-dimethylacetamide as a solvent. (Co) poly(arylene ether sulfone)s showed inherent viscosities in the range 0.92-1.47 dLg⁻¹ and number average molecular weights (M_n), obtained from gel permeation chromatography (GPC, PS standard), were in the range 91,300 – 1,31,000. (Co) poly(arylene ether sulfone)s could be cast into tough, transparent and flexible films from chloroform solutions. X-Ray diffraction studies indicated amorphous nature of (co) poly(arylene ether sulfone)s. (Co) poly(arylene ether sulfone)s showed T_g values in the range 179-191 °C. Most interestingly, the pendant furyl groups in (co) poly(arylene ether sulfone)s provide reactive sites for click modification and cross-linking *via* Diels-Alder reaction with maleimides and bismaleimides, respectively. Cross-linked (co) poly(arylene ether sulfone)s were prepared by the Diels-Alder reaction of furyl containing (co) poly(arylene ether sulfone)s with bismaleimide at 60 °C and the crosslinked polymers underwent retro Diels-Alder reactions at 120 °C. These (co) poly(arylene ether sulfone)s containing pendant furyl groups are potentially useful as self-healable materials.

SYNTHESIS OF EPOXIDIZED SOYBEAN OIL BASED POLYOLS AND EXAMINATION OF THEIR FLAME RETARDANCY

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A significant drawbacks to many polymers are their flammability and their petroleum based raw materials. The use of petrochemicals has some disadvantages in terms of energy, production, and transportation

oils available in most parts of the world. Epoxidized soybean oil (ESO) can be derived by chemical oxidation of soybean oil and is commercially available [2].

Another problem of polymers' is flammability. Flame-retardant additives are often used and necessary for the finished commercial polymer based materials. Today, halogenated compounds for flame retardancy are mainly used in the industry. Halogenated organic molecules, such as brominated or chlorinated compounds, are particularly effective flame retardants. However, they cause environmental and health hazards that are restricting their continued use in the industry[3]. Due to health and environmental causes new flame retardant compounds are significant. Halogen-free flame retardants for polymeric materials have attracted increasing attention in recent years. Especially, phosphorus-containing flame retardants give off less toxic combustion products, influence the reaction in the condensed phase, and become an important replacement for halogen flame retardants[4].

This research focuses on the design and synthesis of novel polymer materials through the incorporation epoxidized soybean oil and phosphorus containing new product into the polymer structure to be used as non-flammable and biodegradable polymers. This work is centered around the synthetic challenges of creating new well defined systems and their potential for advancing in the field of ultra high flame retardancy with an improvement performance for new applications.



Fig. 1: Schematic representation of epoxidized soybean oil based flame retardant polyol.

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Synthesis of new bio-sourced polymers starting from glycerol-based DiVinylGlycol

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Synthetic polymers have become an integral part of our modern technological society. Due to the depletion of fossil resources and to environmental concerns, the synthesis of sustainable polymers from renewable feedstock is today an emerging field. DiVinylGlycol (DVG), a C6 vicinal diol produced from glycerol, represents one potential molecule platform to provide original bio-sourced polymers. In this study, the polymerizability of DVG through various polymerization methodologies was investigated in order to design new bio-sourced polymers with original physico-chemical and thermo-mechanical properties. Hence, we recently investigated the synthesis of bio-based polyesters and copolyesters using different di-esters to form polymers with pendant vinyl groups. In this presentation, we will discuss the synthesis of this new polymers and the study of their thermo-mechanical properties, then the post-functionalization of the pendant double bonds will be broached.

Fatty acid-based Vinylogous Urethane Vitrimers: Controlling the Viscoelastic Properties via Catalysis

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Vinylogous urethane vitrimers are polymer networks that can undergo rapid network rearrangements through swift addition/elimination reactions of free amines resulting in fast stress relaxation and viscoelastic flow at elevated temperatures. In this work, Pripol 2033 and Priamine 1017, two compounds derived from fatty acids, are combined with tris(2-aminoethyl)amine to form the vinylogous urethane network. Additionally, it is possible to control the exchange of the covalent bonds. Simple additives like acids and bases, such as pTsoH and triazabicyclodecene, have been incorporated, which were found to significantly influence, respectively speed up and slow down the kinetics of the covalent exchange reaction on a molecular level leading to a wide range of viscoelastic properties on a material level. This strategy thus offers exquisite control over the viscoelastic properties of the vinylogous urethane materials, enabling the rational design of vitrimer elastomers with short relaxation times at elevated temperatures, aiding the reprocessability of these materials.

Tandem hydroformylation/hydrogenation of natural oil derived substrate and catalysts recycling through crystallisation

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Castor oil contains mainly ricinoleic acid, which can be thermally cracked into undecenemethyl ester. This reagent is hydroformylated using an *in situ* rhodium prepared catalyst, leading to an ester-aldehyde. The latter one is immediately hydrogenated to the corresponding ester-alcohol using an *in situ* prepared Shvo catalyst. The overall process lasts only one hour at 150°C. The mixture is then extracted from the autoclave and transferred into a crystallisation glassware under inert conditions. After being cooled down to -15°C, the ester-alcohol crashes out as fine crystals. The remaining solution containing the catalysts is then filtered out and stored into a Schlenk flask under inert conditions. Undecenmethyl ester is then introduced into the flask and the mixture is transferred to the autoclave through canola. The desired reaction product is solvated with a solvent and extracted from the crystallisation glassware. The autoclave is pressurised with synthesis gas and heated up to 150°C for an hour. The overall process is then repeated, and the catalysts can then be recycled four to five times.

Therefore, we have proven feasible a new way of recycling catalysts using crystallisation techniques.

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Photopolymerization of acrylated methyl ricinoleate

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An efficient synthesis and photopolymerization of acrylated methyl ricinoleate (AMR) was investigated. At the first step of the study, methyl ricinoleate (MR) was synthesized by two-step base catalyzed transesterification reaction. Then MR was acrylated by acryloyl chloride. The bulk photopolymerization of AMR was performed in the presence of 2,2-dimethoxy-2-phenylacetophenone (DMPA) as photoinitiator under UV irradiation at 365 nm. High monomer conversion was achieved with very low initiator concentration. Even with 0.4 % of DMPA, polymer was obtained with a high conversion (42 %). After polymerization reaction, yellow transparent cross-linked polymers were obtained. Polymer gel was characterized by FTIR and NMR Spectroscopy. Thermal characterization of the materials synthesized was revealed by TGA and DSC techniques.

Facile Synthesis Of Pristine Graphene-Palladium Nanocomposites With Extraordinary Catalytic Activities Using Swollen Liquid Crystals.

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Amazing conductivity, perfect honeycomb sp^2 arrangement and the high theoretical surface area make pristine graphene as one of the best materials suited for application as catalyst supports. Unfortunately, the low reactivity of the material makes the formation of nanocomposite with inorganic materials difficult. Here we report an easy approach to synthesize nanocomposites of pristine graphene with palladium (Pd-G) using swollen liquid crystals (SLCs) as a soft template. The SLC template gives the control to deposit very small Pd particles of uniform size on G as well as RGO. The synthesized nanocomposite (Pd-G) exhibited exceptionally better catalytic activity compared with Pd-RGO nanocomposite in the hydrogenation of nitrophenols and microwave assisted C-C coupling reactions. The catalytic activity of Pd-G nanocomposite during nitrophenol reduction reaction was sixteen times higher than Pd nanoparticles and more than double than Pd-RGO nanocomposite. The exceptionally high activity of pristine graphene supported catalysts in the organic reactions is explained on the basis of its better π interacting property compared to partially reduced RGO. The Pd-G nanocomposite showed exceptional stability under the reaction conditions as it could be recycled upto a minimum of 15 cycles for the C-C coupling reactions without any loss in activity.

New Bio-Based Polyurethane Organogelators: Synthesis and Characterization

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New polyurethanes were synthesized from ω -hydroxyacylazides as A-B monomers which in turn were obtained from non-edible renewable resources¹. Specifically, lignin-derived syringic acid, vanillic acid and ω -haloalkanols were used as the starting materials. ω -Haloalkanols used were 6-chlorohexanol and 11-bromoundecanol, which have their origin in bio-derived chemicals viz. adipic acid or 5-hydroxymethyl furfural and castor oil, respectively. These bio-based A-B monomers containing acyl azide and hydroxyl group were self polycondensed to afford polyurethanes which exhibited reasonably high molecular weights ($\eta_{inh} = 0.41\text{--}0.69\text{ dL g}^{-1}$ and $M_n, GPC = 20,000 - 40,400$) and film forming characteristics. Interestingly, polyurethane based on A-B monomer derived from vanillic acid and 11-bromoundecanol exhibited thermoreversible gelation at ambient temperature in polar solvents such as tetrahydrofuran (THF), *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc), *N*-methylpyrrolidone (NMP) and dimethyl sulfoxide (DMSO). DMF was selected as a solvent for in-depth study of phenomenon of organogelation. The gelation behavior of polyurethane in this solvent was attributed to the combined effect of hydrophobic interactions and N-H...O hydrogen bonding². Gel-sol-gel phase transitions, studied by temperature ramp test, indicated that the network formed in gel sample was reversible ($C_p = 3\text{ wt \%}$ in DMF, $T_{gel-sol} = 57\text{ }^\circ\text{C}$, $T_{sol-gel} = 30\text{ }^\circ\text{C}$). G' was independent of applied frequency and G'' showed minima in oscillatory shear measurements indicating the characteristics of soft solid-like material. Further analysis of oscillatory shear data showed that modulus increased with polymer concentration. Gel-sol-gel phase transitions and mechanical properties of polyurethane organogelators were dependent on polymer concentration and solvent polarity.

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Synthesis of Simple Chemical Building Blocks from Algae Oil

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Microalgae and other single cell oils are attractive as a source of chemicals, as they can provide unique fatty acid compositions. In this, algae oil especially has some interesting features. The composition of the algae is rather unique compared to the composition of plant oils. Prominent examples are palmitoleic acid (16:1) and eicosapentaenoic acid (20:5, EPA).^[4] These fatty acids are most interesting for production of building blocks towards chemical materials.

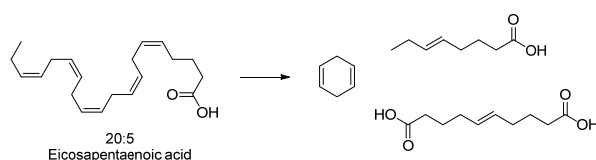


Figure 1. Self-metathesis of EPA and the resulting products.

On the other hand, such fatty acids can be enhanced with the fatty acid composition by genetic engineering. On the other hand, they will be present in a certain extend in feedstock stream if they were to be produced from such alternative sources on a larger scale. ^[1] Naturally, these double bonds can be exploited by multiple functionalization reactions such as carbonylation, ozonolysis or addition reactions. One major drawback in this is that these reactions will not be very selective and remain to be difficult to induce selectivity. However, a possibility to convert EPA selectively for production of chemicals would be via olefin-metathesis. Here, intramolecular metathesis overrules intermolecular metathesis which leads to the formation of 1,4-cyclohexadiene as major component. Combining the metathesis directly with a dehydrogenation step provides benzene from a renewable resource. The other product(s) will either be an unsaturated mono-ester, or an unsaturated di-ester. The unsaturated mono-ester can be directly used in a follow up alkoxy carbonylation, providing the saturated di-ester (Figure 2). Both the unsaturated di-ester and saturated di-ester can be directly used as building blocks in polymerization reactions. Employing olefin-metathesis as modification step furthermore attractive due to the high activity of metathesis catalysts, and the selectivity towards the products.

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Combination of different methods of liquid chromatography for the analysis of glycerol products oxidation

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The oleo-chemical reactions carried out on natural fats and oils have many advantages such as the creation of biofuels, the preparation of soaps, fatty acids, fatty acid methyl esters. These transformations allow the production of glycerol as co-product. In fact, since the last ten years, glycerol is considered as one of the 12 renewable key building blocks, with great promise in terms of the sustainability, cost and versatility. So, oxidation platforms have been developed and adapted on glycerol to try to satisfy a demand into organic acids for green chemistry. For example, Dihydroxyacetone is used in cosmetic industry, as saying hydroxyl-acids such as oxalic acid or glyceric acid that are chelating molecules which can be used as nutritional supplements for the crop. It exists different synthesis for the oxidation of glycerol: biological (for example the use of glyoxal oxidase¹ or with microorganism²), chemicals with particles of gold/platinum³, or with the use of polyoxometalate like Na₄W₁₀O₃₂⁴. But in actual publications, it was not offered a confirmation of the structure of each glycerol oxidation product: confusion between different products was possible. In fact, High Performance Liquid Chromatography (HPLC) is the main method used for simultaneous identification of glycerol oxidation products, from reactional or standards mixture.

In addition, some publications using Aminex HPX 87 H present chromatograms of oxalic acid with a very good resolution⁵. We repeated the experimental conditions cited but we didn't get the same results. In the same way, other works present results about oxalic acid but they don't allow associated chromatogram molecule⁶. So, we suggest to use the HPIC (ICS 2000, Thermofisher) with column AS 11- HC (Dionex) with multistep gradient of NaOH for the analysis of dicarboxylic acid from glycerol oxidation mixture, like tartronic and oxalic acid to obtain good definition and quantification for these acids. Therefore, our work suggest the use of Aminex HPX-87H (Biorad) for: firstly a usual analysis with HPLC (H₂SO₄ 3mM, 60°C) and a comparison with known standards for a rapid identification and quantification; secondly a fraction collection with a semi-preparative module (0.1% formic acid 56°C); thirdly, fractions obtained were analyzed by Electrospray LC (with an orbitrap analyzers) and by RMN.

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Synthesis and properties of new functionalized bio-based estolides

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In recent years, the awareness and the concern about fossil resources and their impact on the environment have led to a growing interest in the use of renewable resources in polymer and material fields. Because of their competitive cost, their worldwide availability and their built-in functionalities, vegetable oils, which are annually renewable, are an attractive raw material for polymer chemistry.^{1,2}

Vegetable oil derivatives, as fatty acids, appear as a large chemical platform for new and innovative bio-based polymer materials, such as a class of polyesters named *estolides*, obtained by auto-condensation of an alcohol on the ester functional group of the AB-type fatty acid monomer.

Estolides, already used in cosmetic and industrial applications, have interesting properties, such as good behavior at low temperature, oxidative resistance and biodegradability.³

In this study, functionalized estolides from ricinoleic esters have been obtained by thiol-ene derivatization of the double bonds. It is therefore possible to fit the properties of the estolides to a given application, broadening the potential markets of this family of bio-based polymers.

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First Row Transition Metal Catalyzed One-Pot Oxidative Cleavage of Unsaturated Fatty Acids

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Biomass has been identified as a prime candidate to replace fossil resources as the feedstock for the chemical industry. Unsaturated fatty acids (UFAs) are widely used for producing valuable industrial materials through their oxidative modification. One example is the synthesis of mono- and dicarboxylic acids *via* oxidative cleavage. This process is predominantly done using ozone in industry. However, the hazardous problems associated with ozonolysis still remain controversial. Catalytic processes for oxidative cleavage of UFAs have been investigated in order to replace ozone, which are mainly based on the use of scarce and generally toxic second and third row transition metals (Ru, Os, Pd, etc). Clearly, the use of first row transition metal-based catalysts would be more preferential due to their ready availability, low price and low toxicity.

In this presentation, first-row transition metal (Fe or Mn) based catalytic systems for the oxidative cleavage of UFAs and esters have been developed with H_2O_2 and NaIO_4 as oxidants (Figure 1). These systems operate under mild reaction conditions and at low catalyst loadings, and are able to achieve excellent product yields through a three-step, one-pot procedure. The aldehyde products are of interest in industrial and medical uses.

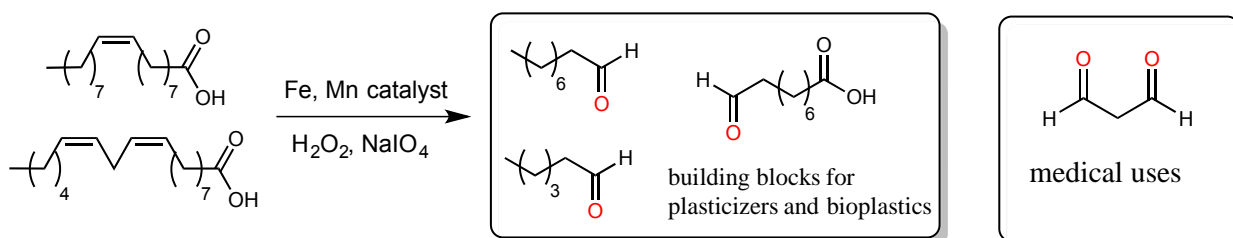


Figure 1. Oxidative cleavage of UFAs initiated by Fe (or Mn) / H_2O_2 catalytic systems.

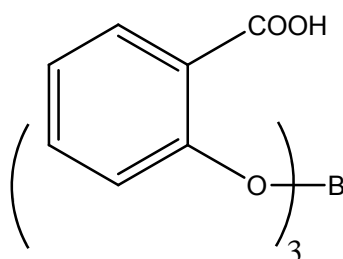
Polymerization of Epoxidized Soybean Oil with Carboxyl Functionalized Boron Esters

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Epoxidized soybean oil (ESO) is one of the most used plant oil based monomers. It is directly obtained from the epoxidation of soybean oil. Many reactive monomers and polymers can be synthesized from ESO by the reaction of oxiranes of ESO with different functional groups such as carboxylates, phenols, thiols and amines. Many works can be found in the literature about the polymerization of ESO with carboxylic acids. Alpha hydroxy carboxylic acids (AHA) are special compounds that are found in nature. Salicylic acid, lactic acid and tartaric acid are the most common α -hydroxy carboxylic acids. These compounds do not give polymers when they are reacted with ESO although their boron esters give. When α -hydroxy carboxylic acids are refluxed with boric acid in an inert solvent, the hydroxyl groups are esterified with boric acid. The resulting boron esters contain free carboxyl groups. These esters can be used for curing of ESO. After polymerization reaction, rubbery materials are obtained.



Tri salicyl borate

Structure of boric acid ester of salicylic acid

CALB as an efficient catalyst for a greener production of biosurfactants: screening of the main influent parameters and optimization

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Fatty acid sugar esters find a wide range of commercial applications in food, cosmetic and pharmaceutical industries due to their surfactant properties. They can be synthesized using enzymatic catalysis (usually using lipase), which is chemoselective and carried under mild conditions, but results in slower and lower conversions than chemical catalysis, and usually requires important amounts of lipase (around 20% wt/wt of supported lipase).

In this work, synthesis of fatty acid glucose esters under lipase catalysis was studied and the main influent parameters were screened in order to optimize the conversion into sugar ester with the minimum amount lipase. In all cases, only 6-O-monoester of glucose was obtained. *Candida antarctica* B (CALB) was found to be the most efficient lipase and acetonitrile the most suitable solvent. We obtained far better results than what can be found in literature : the use of only 5% wt/wt of CALB in acetonitrile at 45°C was sufficient to lead to a full conversion into 6-O-monoester within 40 hours without any shift of the equilibrium by water removal.

Then the influence of the acyl donor was studied: kinetics studies were performed on fatty acids (FAs) from C8 to C18 and fatty acid vinyl esters (FAVEs) from C4 to C18, and the results were compared : Starting from FAs, kinetics and conversions were increasing with the chain length, highlighting a preference of CALB for long chain substrates. Quite different results were obtained with FAVEs : Long chain FAVE led to the a full conversion into sugar esters; the highest conversion rates were observed for the shortest FAVE but competitive hydrolysis of the so-formed sugar esters into fatty acids was also observed and the conversion decreased after reaching a maximum.

Modification of Cellulose via Ugi 5CR in CO₂ switchable solvent

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Most of the raw materials used in the chemical industry are petroleum derived. Since petroleum is depleting and unsustainable, an increasing drive towards the use of sustainable alternatives is observable. Cellulose is the most abundant organic bio-based material with established uses as raw material in the chemical industry. However, the vast potential of this versatile material is limited by its insolubility. Recently, ionic liquids have been described as “green” solvents for cellulose solubilisation. However, we have shown in the course of this project that EMIMAc (1-Ethyl -3-methylimidazolium acetate), which is the most widely reported ionic for cellulose solubilisation, is not suitable for modification of cellulose via the direct Ugi-5 component reaction (Ugi 5-CR). Furthermore, in order to improve the sustainability of our project, we are now investigating CO₂ switchable solvents for cellulose solubilisation and subsequent modification via Ugi 5-CR. This solvent system offers advantages to traditional ionic liquids: it can solubilise cellulose within 10 min at fairly low temperature (50°C) and the precipitation/regeneration of cellulose can be achieved by simply releasing the CO₂. Via Ugi 5-CR, we are thus able to use the inherent –OH groups in cellulose alongside CO₂, a carbonyl, isocyanide and an amine to introduce a carbamate protected amino amide functionality into cellulose backbone directly without any activation. Finally, we aim to evaluate the influence the various functional groups on the mechanical and thermal property of the modified cellulose.

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Chain Multiplication of Fatty Acids

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Ultra Long-chain α,ω -difunctional building blocks represent an interesting class of substrates and are often found in nature as structure-bearing elements. For instance, they occur as ceramide – a major component of the *stratum corneum* of the epidermis layer of the human skin, and they are part of the cellular walls of several algae species (algaenans) but also of plants (cutin and suberin). Further, such chain lengths correspond to the typical lamella thickness of polymer crystals, rendering them relevant for convenient access to nanocrystals and to high-melting polymers.

The preparation of ultra long-chain α,ω -difunctional building blocks is possible by various approaches to date. However, conventional routes *via* traditional organic synthesis require elaborate multi-step reactions and involve stoichiometric side products. A more straightforward approach is the utilization of fatty acids from plant oils as they inherently provide a long aliphatic methylene sequence. A major drawback of most state-of-the art techniques though is that the maximum chain length accessible is in the same range as the fatty acid used.

We report a novel approach for the chain-length multiplication of monounsaturated fatty acids by a combination of two catalytic transformations, namely olefin metathesis and double-bond isomerization. With this unique process, ultra long-chain α,ω -difunctional building blocks with a doubled methylene sequence are obtained. Starting from readily available oleic acid (18:1) and erucic acid (22:1) this translates to the formation of C₃₂ or C₄₈ building blocks. For example, HOOC-(CH₂)₄₆-COOH is accessible in 99% purity *via* this scalable approach. As a possible application of such ultra long-chain compounds the preparation of high-melting polyesters (up to T_m = 120 °C) is reported. Furthermore these well-crystallizable compounds offer themselves for the preparation of thermoplastic elastomers or polymer nanocrystals.

Organocatalyzed non-isocyanate polyurethane (NIPU) coatings from bio-based cyclic carbonates

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Polyurethanes (PU) are highly versatile materials used in widespread industries such as automotive, building, construction, and packaging. They have also been used in the medical field as flexible and rigid foams, adhesives, coatings, thermoplastic, or thermoset materials. Traditionally, PUs are synthesized from polyols and isocyanates. Concerns on the use of isocyanates as starting materials have risen due to the fact that their synthesis involves the use of phosgene. In order to circumvent this issue, much research has been devoted to exploring alternative approaches to the synthesis of PUs. Non-isocyanate polyurethane (NIPU) synthesis using cyclic carbonates has gained popularity as one of the new approaches.

In this study, novel bio-based resins are synthesized by converting epoxidized sucrose soyate (ESS) into carbonated sucrose soyate (CSS) under super critical conditions. Initial studies have shown promise in systems where CSS is crosslinked with multifunctional amines generating coatings with good solvent resistance. The effect of organocatalysts was studied and formulations of bio-based non-isocyanate polyurethane coatings were developed.

Tunable polymer films obtained from allylated lignin and plant oils *via* cross-metathesis

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Lignin is one of the most abundant biopolymers on earth and thus a highly available renewable resource.^[1] Especially for the production of aromatic compounds, lignin probably is the most promising alternative to petroleum-based materials. The functionalization of both the phenolic and aliphatic hydroxyl groups in lignin is essential for material properties of the macromolecular structure for application in polymer chemistry.^[2]

The alkylation of phenols with organic carbonates was shown to be a non-toxic, sustainable and effective alternative to conventional Williamson ether synthesis. It is already well established for different phenols that can serve as model substances for phenolic hydroxyl groups in lignin.

Efficient allylation with diallyl carbonate of both, aliphatic and aromatic, hydroxyl groups of organosolv lignin (OL) was shown in detail.^[3] The product was used as cross-linker with different plant oils *via* cross-metathesis curing. Depending on the lignin-to-plant oil ratio as well as the nature of the oil, the material properties varied from brittle to ductile. Thus, tunable polymer films were obtained.

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Multi-enzyme cascades for the derivatization of bio-based molecules

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Alkenamines are chemical intermediates for the production of active pharmaceutical ingredients, fine chemicals, in cosmetic industry, cleaning agents or plasticizing agents. Industrial production of alkenamines takes place synthetically starting from a petrochemical raw material. However, the chemical approaches often suffer from severe drawbacks such as harsh reaction conditions, use of toxic transition metal catalysts and sometimes insufficient stereoselectivity in a single catalytic step, causing environmental issues.

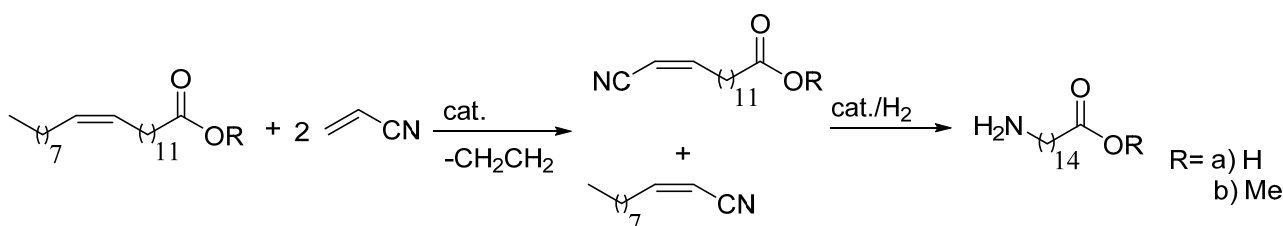
In this project we developed an in vitro reaction cascade for the production of alkenamine starting from renewable resources such as the hydroxylauric acid obtained from plant oil. The experimental system consists of three enzymatic steps, to which additional enzymes for cofactor regeneration will be added. The first step is the decarboxylation of fatty acids with H₂O₂-dependent P450 fatty acid decarboxylase OleT_{JE}. Since the large amount of H₂O₂ has a toxic effect on the enzyme, an in situ light-driven H₂O₂ regeneration system is carried out. The oxidation of the alcohol to the aldehyde is catalyzed by a NADP⁺-dependent alcohol dehydrogenase. The ω-transaminase catalyzed then the third step, the formation of alkenamines.

This reaction system is an environmentally friendly alternative of alkenamine synthesis in comparison to the traditionally production of this chemical. The poster presents each individual reaction step and describes the results of the biocatalysis.

From Plant to Plastic: Synthesis of renewable polyamide-15 building block from erucic acid

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A valuable route to obtain nitrogen-containing molecules is via the cross-metathesis of acrylonitrile with olefins.¹ Recently, the cross-metathesis of fatty acid derivatives with acrylonitrile – which has become a sustainable raw material² – has been demonstrated (Scheme 1).³ This cross-metathesis is a key reaction for the synthesis of linear amino acid derivatives, synthesized via hydrogenation of the intermediate unsaturated α,ω -cyano-acids or esters. These linear amino acid derivatives can be used as renewable building blocks for the synthesis of polyamides.



Scheme 1: Cross-metathesis of erucic acid with acrylonitrile and subsequent hydrogenation of the resulting unsaturated α,ω -cyano-acid.

During this research the synthesis of 15-aminopentadecanoic acid via the cross-metathesis of technical erucic acid with acrylonitrile and subsequent hydrogenation of the resulting unsaturated α,ω -cyano-acid was investigated. 15-Aminopentadecanoic acid was successfully synthesised leading to an isolated yield of 37% after column chromatography. Meanwhile, parameters of both reaction steps were optimized leading to lower catalyst ratios.

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From unsaturated fatty acids to linear dicarboxylic acids: A direct access by isomerizing hydroxycarbonylation

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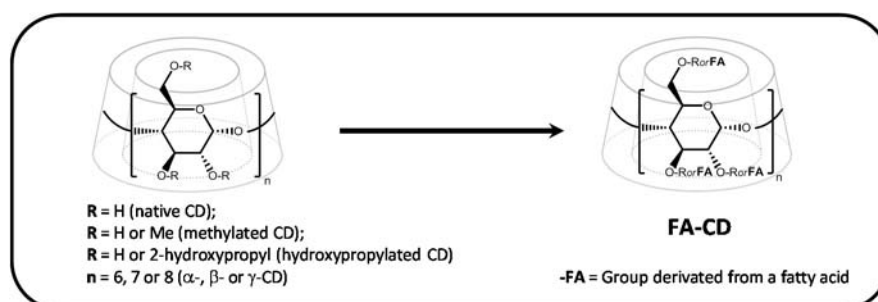
Dicarboxylic acids are valuable intermediates with many applications. Adipic acid, used on a very large scale for the production of nylon-6,6, and sebacic acid, used in corrosion protection and also nylon production, are prominent examples. However, unlike their shorter chain congeners, long-chain linear dicarboxylic acids have been difficult to access in a direct way to date.

In this contribution, we present the direct generation of long-chain α,ω -dicarboxylic acids by catalytic isomerizing functionalization of unsaturated fatty acids and plant oils. The double bond deep in the fatty acid chain is selectively carbonylated with water as a nucleophile to a terminal carboxy group. This reaction is applicable to a wide range of substrates, e.g. mid-chain fatty acid derivatives like 10-undecenoic acid and long-chain oleic and erucic acid. Even technical grade plant oils, like high oleic sunflower oil can be hydrolyzed and hydroxycarbonylated in one step toward the linear, long-chain dicarboxylic acid. Identified key elements of this reaction are a homogeneous reaction mixture that ensures sufficient contact between all reactants and a catalyst system that allows for activation of the Pd-precursor under aqueous reaction conditions. A relatively small nucleophile concentration and an incomplete formation of the catalytically active Pd-hydride species limit the potential of the reaction. Additionally, the rates are limited by a high energetic barrier for the hydrolysis, as identified by DFT calculations. Nevertheless, the isomerizing hydroxycarbonylation of unsaturated fatty acids ranks as one of the most active isomerizing functionalization reactions in combination with remarkable selectivities above 90% toward the valuable linear dicarboxylic acids.

Fatty acid-modified cyclodextrins as mass transfer promoters for aqueous rhodium catalyzed hydroformylation

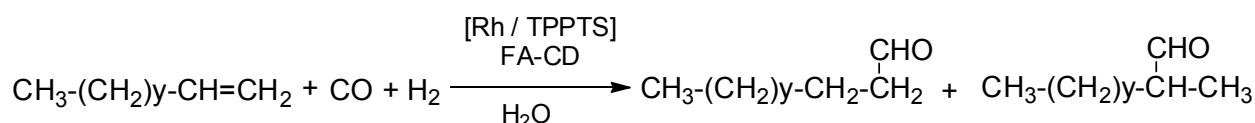
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New cyclodextrins called **FattyAcid-CycloDextrins (FA-CDs)** have been synthesized in high yields starting from native or modified CDs.



The synthesis protocol allowed to easily modulate the nature of the CD, the type of the fatty acid derivatives and the substitution degree (*i.e.* the number of **-FA** group grafted per CD). These modified CDs have shown good solubilities in water as well as aggregation properties.

Tested as mass transfer promoters [1,2] in 1-hexadecene and 1-decene aqueous biphasic hydroformylation catalyzed by a [Rhodium/TPPTS] system (TPPTS = tris(*m*-sodiosulfonatophenyl)phosphine)), these cyclodextrins led to very fast reactions.



These very good catalytic results were attributed to the inclusion, tensioactivity and aggregation properties of these new chemically modified cyclodextrins.

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SLE diagram for a high oleic palm oil based fatty acid mixture at low saturated content

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Vegetable oils and their derivatives are increasingly replacing mineral oils in their applications.[1,2] Among other constituents in vegetable oil, both saturated and unsaturated fractions are important raw materials. The latter possesses double bonds which can provide as substrates or raw materials for various chemical industries.[3] Fractionation of these oils or as in our case the Poly-Unsaturated Fatty Acid (PUFA) mixture is required so as to generate favorable compositions according to applications. Generation of Solid Liquid Equilibrium (SLE) phase diagrams for real mixtures is extremely important to enable a thorough understanding of the thermodynamics of the fractionation process of crystallization.

The PUFA mixture was fractionated in a multistage scrubbing layer crystallizer. The product was put into a decanter centrifuge so as to fractionate them into mother liquor and crystal fraction. The temperature in the jacket was maintained such that $\Delta T < 5K$ from the liquidus point obtained from the Differential Scanning Calorimeter (DSC) thermal analyses. Each crystallizer was also maintained at a temperature 5K below the previous one. This way a slow and successive cooling of the PUFA was achieved such that probes from different fraction could be obtained. They were analyzed thermally and chemically in the DSC and Gas Chromatography – Flame Ionization Detector (GC-FID) setup respectively.[4]

Similar to previous literature as in [5], technically relevant partial SLE diagrams for high oleic palm oil was created by fractionating the mixture in a scrubbed layer crystallizer along with their metastable range were determined.[6]

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Controlled Radical Polymerization of Polymeric Linoleic Acid with Styrene and Pentafluorostyrene

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The initiated polymer chains are reversibly capped by a stable-free radical, such as 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO), to provide a dormant living polymer. Reversible activation deactivation of the chain end provides control over the polymerization of monomers, such as styrene [2-4]. In this study the polymeric fatty acids for use in controlled polymerization in the presence of 2,2,6,6-Tetramethylpiperidinoxy (TEMPO) was investigated. Thus, two block graft copolymers PLina-g-Poly (styrene) and three block graft copolymers PLina-g-Poly (styrene)-g-Poly (pentafluorostyrene) were synthesized [1]. The reaction mechanisms and kinetics were examined. The all graft copolymers obtained were characterized by proton nuclear magnetic resonance (¹H NMR), ¹⁹F NMR and gel permeation chromatography (GPC).

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Synthesis and Characterization of Graft Copolymer Based Polymeric Fatty Acid Using Free Radical Polymerization and the Ring Opening Polymerization

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This polymeric fatty acid which has peroxide and carboxylic acid groups was used as free radical polymerization (SRP) and the ring opening polymerization (ROP). The graft copolymers were synthesized both methods. Also, the polymerization process using a combination of both (one- pot polymerization) of the new graft copolymers were synthesized. Using a ring opening polymerization, two block graft copolymers were synthesized as PLina-g-Poli (caprolactone), graft copolymers, using a free radical polymerization, two block graft copolymers were synthesized as PLina-g-Poly (styrene), three block graft copolymers were synthesized as PLina-g-Poly(styrene)-g-Poly(caprolactone). Polymerization time, monomer concentration, initiator concentration, and basic parameters were determined. The obtained graft copolymers were characterized by ¹H-NMR and DOSY-NMR spectroscopy, gel permeation chromatography (GPC), thermal gravimetric analysis (TGA) and differential scanning calorimetry techniques (DSC).

Acknowledgments: This work was supported financially by the Turkish Scientific Research Council (Grants Numbers: 110T884), the Duzce University Research Fund (Grant Number: 2016.07.06.487, 2015.05.03.381).

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One Pot Synthesis of Oil-Based Graft Copolymers by Using ATRP and ROP

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One-pot synthesis of graft copolymers by ring-opening polymerization atom transfer radical polymerization using polymeric linoleic acid peroxide (PLina) is reported. The hydroxylated polymeric fatty acids, atom transfer radical polymerization (ATRP), and using a combination of both ATRP both SRP various graft copolymers were synthesized. Using only ATRP, PCL-g-PSty diblock graft copolymers were synthesized. Using a one-pot method PLina-g-PCL-PSty, triblock graft copolymers were synthesized. Polymerization time, monomer concentration, initiator concentration, and basic parameters were determined. The obtained graft copolymers were characterized by ¹H NMR spectroscopy, gel permeation chromatography (GPC), thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC).

Acknowledgments: This work was supported financially by the Turkish Scientific Research Council (Grants Numbers: 110T884), the Duzce University Research Fund (Grant Number: 2016.07.06.487, 2015.05.03.381).

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One-Step Synthesis of Poly(linoleic acid)-g-Poly(N-isopropylacrylamide)-g-Poly(D,L-lactide) Graft Copolymers

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One-step synthesis of graft copolymers by ring-opening polymerization and free radical polymerization by using polymeric linoleic acid peroxide and polymeric linoleic acid peroxide is studied. Graft copolymers having the structure of poly (linoleic acid)-g-p-(N-isopropylacrylamide)-g-poly(D,L-lactid) were synthesized from polymeric linoleic acid peroxide possessing peroxide groups in the main chain by the combination of free radical polymerization of N-isopropylacrylamide and ring opening polymerization of D,L-lactid in one-step. The principal parameters such as monomer concentration, initiator concentration, and polymerization time that affect the one-step polymerization reaction were evaluated. The graft copolymers obtained were characterized by proton nuclear magnetic resonance (¹H NMR), gel permeation chromatography (GPC), thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) techniques. These characterization studies of the obtained polymers indicate graft copolymers easily formed as a result of combination free radical polymerization and ring opening polymerization in one-step.

Acknowledgments: This work was supported financially by the Turkish Scientific Research Council (Grants Numbers: 110T884), the Duzce University Research Fund (Grant Number: 2016.07.06.487, 2015.05.03.381).

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New Partially Bio-based Epoxy Thermosets Starting from Cashew Nut Shell Liquid: Synthesis and Thermomechanical Properties

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A diphenol, namely, 4-(4-hydroxyphenoxy)-3-pentadecylphenol (HPPDP) was synthesized starting Cashew Nut Shell Liquid (CNSL)-a non-edible oil obtained as a byproduct of cashew processing industries. HPPDP was reacted with epichlorohydrin to obtain diglycidyl ether of 4-(4-hydroxyphenoxy)-3-pentadecylphenol- the epoxy monomer containing built-in ether linkage and pendant pentadecyl chain. The curing reactions of diglycidyl ether of 4-(4-hydroxyphenoxy)-3-pentadecylphenol with isophoronediamine (IPDA) and diethylenetriamine (DETA) were studied. Thermal and mechanical properties of the partially bio-based thermosets were investigated. A comparison was made between properties of cured resins based on diglycidyl ether of 4-(4-hydroxyphenoxy)-3-pentadecylphenol with that of diglycidyl ether of Bisphenol-A.

Eco-friendly aerobic oxidation of α -pinene catalyzed by homogeneous and heterogeneous Mn catalysts

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Among other renewable raw materials, terpene feedstocks are a valuable and readily available supply of building blocks for the fine chemical industry. α -Pinene is one of the low-priced monoterpenes, which can be obtained from turpentine. Oxifunctionalization of α -pinene is of high interest, since it yields commercially important intermediates for various flavors, fragrances, pharmaceuticals and chiral building blocks.^[1] The novel Mn-based mixed-linker metal-organic framework MIXMIL-53-NH₂(50)-Mal-Mn was successfully synthesized in a two-step post-synthetic modification reaction and investigated as catalytic material for the liquid-phase aerobic oxidation of α -pinene. Mn(III) acetate was furthermore used as homogeneous model substance. After investigating the influence of reaction time, solvent, temperature, oxidant flow rate and catalyst concentration on conversion, yield and selectivity, optimized reaction conditions were transferred to the heterogeneous MOF-catalyst for direct comparison. In both cases, pinene oxide was obtained as main product along with small amounts of verbenol and verbenone. Using Mn(III) acetate as homogeneous catalyst, after 6 h the α -pinene conversion was up to 62% with 40% pinene oxide yield (GC, 65% selectivity), whereas the oxidation catalyzed by MIXMIL-53-NH₂(50)-Mal-Mn achieved a smaller conversion of 34% and 21% yield (GC, 62% selectivity). The heterogeneous MOF-catalyst was easily removed from the reaction mixture by filtration and reused for at least five catalytic cycles without loss of activity. Hot filtration tests showed that the catalysis mainly proceeds heterogeneously, although the involvement of minor homogeneous species could not be completely excluded.

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A dual catalysis approach: Selective conversion of multiunsaturated fatty acids via hydrogenation and isomerizing alkoxyacylation

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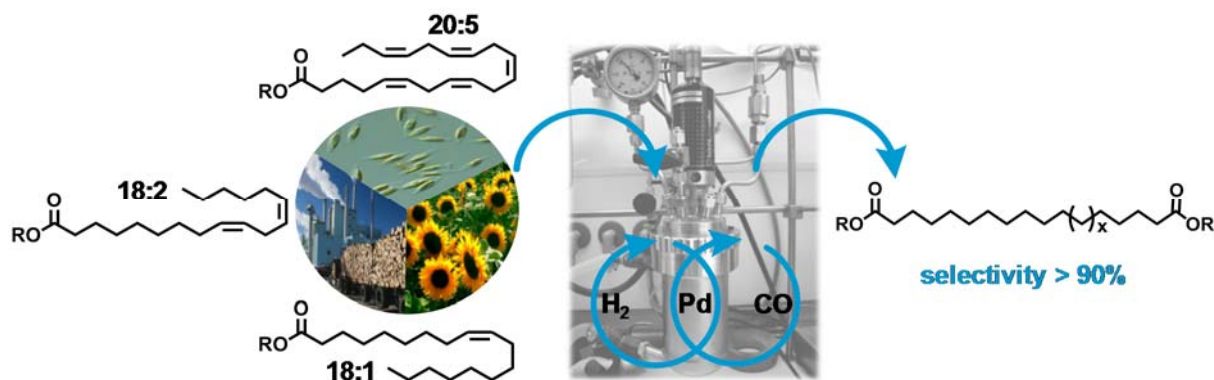
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Unsaturated fatty acids from plant and algae oils are a promising alternative source for the production of chemicals due to their long-chain linear methylene segments in combination with a varying number of reactive double bonds.[1] Additionally, waste materials, like tall oil from the pulp and paper industry, contain similar compounds with this attractive chemical structure.

A conversion to linear α,ω -functionalized compounds is of particular interest, for example, for the utilization as monomers in polycondensation reactions.[2] This requires the conversion of an internal double bond deep in the fatty acid to a terminal functional group in order to incorporate the full fatty acid chain. This can be brought about in principle by isomerization-functionalization approaches, for example with isomerizing alkoxyacylation converting monounsaturated fatty acids to linear α,ω -diesters with high conversion and selectivity. Multiple unsaturated fatty acids, e.g. eicosapentaenoic acid (20:5) present in algae oil, cause a significant decrease in reaction rate, and therefore favor a range of side reactions resulting in a lower selectivity for the desired linear product.[3] In order to circumvent these problems and to make use of the full potential of the multiunsaturated long-chain fatty acids, preceding selective hydrogenation to the monounsaturated derivatives followed by alkoxyacylation, is a suitable strategy for multicomponent fatty acid mixtures.[4]

In this contribution, we present a novel approach of a dual catalysis reaction combining selective hydrogenation and isomerizing alkoxyacylation of a range of renewable resources.

Selective hydrogenation of multiple unsaturated fatty acids can be performed with several heterogeneous metal catalysts supported on various materials [5]. Here, we report about the reconciliation of the selective hydrogenation to monounsaturated fatty acids with the further functionalization. Consequently, these two reactions can be combined to convert multicomponent and multiunsaturated fatty acid mixtures to α,ω -functionalized compounds in high conversion rates and remarkable selectivities.



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Highly efficient Tsuji-Trost allylation of biobased phenols catalyzed by Pd-nanoparticles in water

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The design of a more sustainable future involves the use of catalytic procedures in order to reduce reagent consumption and to prevent wastes. In such procedures, non-toxic solvents and reagents, as well as biobased substrates should be preferred. Tsuji-Trost allylation reactions are key reactions in organic chemistry. Recent research on the topic mainly focuses on the design of new ligands and heterogeneous catalysts to substitute classic homogeneous catalysts for allylic alkylation, such as Pd(PPh₃)₄, which suffers from being expensive, air sensitive, not recyclable and require the use of (often toxic) organic solvents. In this work, palladium nanoparticles stabilized by poly(vinylpyrrolidone) were investigated as catalyst for Tsuji-Trost allylation in water. The efficiency of the catalyst was first tested on several methylene active compounds. Their reaction with allyl methyl carbonate selectively led to di-allylated products in high yields. Very high turnover numbers (up to 200 000) and turn over frequencies (up to 16 000) were obtained. Then, this catalytic system was successfully applied to the allylation of biobased phenols such as eugenol, guaiacol, vanillyl alcohol and 2,6-dimethoxyphenol. With a full conversion reached in few hours and a very low catalyst loading, this approach constitutes a sustainable alternative to classic allylation procedures employing high amounts of bases and toxic reagents, such as allyl halides.

Novel bio-based copolyesters derived from ricinoleic acid

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Bio-based polymers are continuously object of a great interest from both academia and industry due to the increasing need to lower the impact of petrol-based compounds on our society. In this context, plant oils are among the most promising candidates as economical and renewable source of many monomers for bio-polymer production.

Castor oil, derived from the beans of the castor plant, *Ricinus Communis*, of the *Euphorbiaceae* family, contains approximately 85–90 wt% of triglycerides of ricinoleic acid (RA). RA could be a precursor for the synthesis of interesting materials thanks to the presence of hydroxyl and carboxyl groups, as well as a $\Delta 9$ unsaturation. The self-polycondensation of ricinoleic acid produces an amorphous polyester (PRA), characterized by a remarkable biocidal activity and a low T_g, that strongly limits its applications. To overcome these limits, copolymerization can be the synthetic pathway that allows PRA to enhance its poor mechanical properties, maintaining its antimicrobial activity, as already observed for PBS/PRA copolymers.

In this work, PRA has been co-polymerized with vanillic acid, an aromatic hydroxyacid that can be easily produced from lignin. A novel one-pot, sustainable polymerization procedure of vanillic acid with ethylene carbonate has been recently developed for the production of poly(ethylene vanillate), a PET-like polymer, characterized by high thermal transitions, a notable level of crystallinity, and a certain brittleness. Now, the random copolymers between ricinoleic and vanillic acids represent a new aromatic, antibacterial class of polymers that should have potentially applications in active packaging or biomedical sectors.

Application of specialty lipases in chemo-enzymatic processes

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The focus of Enzymicals is to provide integrated solutions for biocatalytic applications, which are dedicated to the design, development and implementation of cost-effective, sustainable and scalable chemo-biocatalytic routes.

What is more, Enzymicals has profound knowledge in the design, production and application of specialty lipases. One example for the application of these lipases is the selective fatty acid separation in natural oils. Further examples include the application of our lipases in chemo-enzymatic processes in kg-scale for the synthesis of modified fatty acids and derived products like biodegradable lubricants.

In addition, we are project partners in two public-funded research projects with focus on sustainable fat and oil processing for future applications: Horizon 2020 COSMOS and BMBF ZeroCarb FP.

Here we present a selection of the industrial applicability of our specialty lipase collection and process development.

Catalytic functionalisation of starch and amylose using plant oils: towards polymeric materials and composites

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Fossil fuels have been the main source of starting materials for the chemical industry over the last century. Especially synthetic polymers rely on this feedstock and are indispensable for mankind's technological advances and *status quo*. However, a shift to renewable and sustainable resources is needed, as the end of the fossil fuel era is in sight. Biomass presents one possible alternative to fossil fuels, as it consists of a large pool of different chemicals and is inexhaustible. Cellulose, and the closely related starch and amylose, are available cheaply from plants and have favourable properties, such as high strength, thermal stability and biodegradability. However, such poly(saccharides) have been difficult to use directly as materials because of the lack of thermoplasticity, low solubility and high hydrophilicity. Modifications are thus necessary to be able to exploit their advantageous properties. Recently, our group published the catalytic transesterification of maize starch with different plant oils to obtain fully renewable fatty acid starch esters in a sustainable fashion. Polymeric materials with glass transition temperatures (T_g s), soluble in common organic solvents and an increased hydrophobicity were obtained. Compatibilisation tests of the modified starch and amylose with low-density poly(ethylene) (LDPE) and cellulose are being investigated to obtain composites of commodity plastics with improved mechanical properties.

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Sustainable functionalization of bacterial cellulose for the design of innovative bio-based nanomaterials

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Bacterial cellulose (BC) is a unique nanocelulose form, produced by *Acetobacter Xylinus* bacteria (Fig. 1), which, due to its unique properties (biodegradability, water-holding capacity, biocompatibility, high mechanical strength and good elastic properties) has

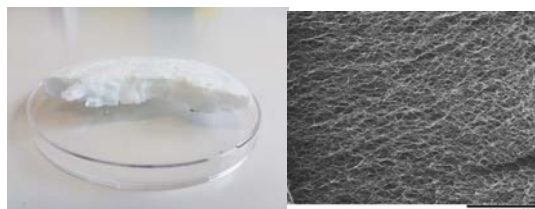


Figure 1: Image of freeze-dried BC's section (left), SEM picture X2000 of BC's section (right)

already found applications in food industry, wound dressing and surgery. In addition, the heterogeneous functionalization of bacterial cellulose might induce innovative functional properties while preserving its unique tridimensional network. This PhD project intends to develop new strategies for the heterogeneous functionalization of BC using green and sustainable conditions, aiming at producing new functional materials with antimicrobial properties for medical applications. Bacterial cellulose's bioactivity will be achieved by the coupling of a lantibiotic peptide, called nisin. This bacteriocin as large spectra of activity against Gram+ organisms such as *Staphylococcus aureus*, *Listeria monocytogenes* and *Pseudomonas spp.* The coupling of Nisin on BC's surface has been investigated via three routes: chemical coupling with and without a linker and enzymatic coupling with a linker. The linker chosen in this project is the aminopropyl trimethoxysilane (APTMS) in which silanes can silylated BC and amino groups can react with the primary amines or the carboxylic acid of nisin. For this presentation, we are going to focus on the silylation of BC by APTMS (Fig. 2) and on the chemical coupling between BC and Nisin by using APTMS as a linker (Fig. 3).

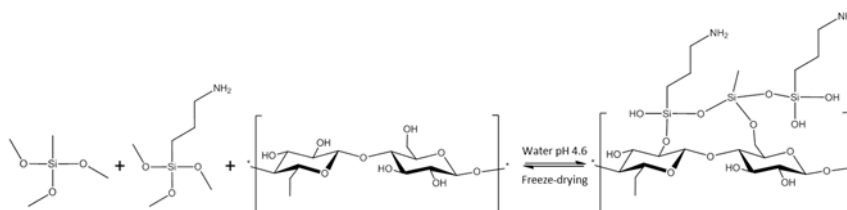


Figure 2: Silylation of BC

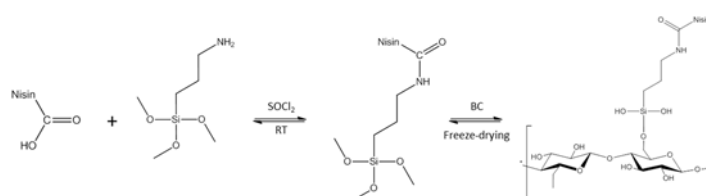


Figure 3: Mechanism of the grafting of Nisin on BC by using APTMS.

Life Integrated Process for the Enzymatic Splitting of triglycerides

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The goal of the **LIPES** project is to enzymatically produce selected commercially important fatty acids at an overall lower variable cost than the current processes and to showcase their use as intermediates in a wider range of applications. The project rationale originates from the need to produce higher quality fatty acids to widen their applicability over a broader range of end-products, reach higher value products and in a more sustainable way.

LIPES aims to perform the scale-up to pre-industrial level of a new environmentally friendly alternative to the traditional and current splitting routes of triglycerides, at a lower variable and investment cost and in a very resource-efficient way with a minimum saving of 45% water consumption, 70% enzyme use and 80% energy consumption.

The **LIPES** project gathers partners covering the whole value chain with Oleon and DSM producing chemical intermediate and end products (respectively esters and polymers) in different market segments, STC as an engineering company specialized in mixing technology and reactor design, Biocatalyst as an innovative enzyme producer and TUB as a renowned specialist in fluid dynamics. This project has received funding from the Bio Based Industries Joint Undertaking under the European Union's Horizon 2020 research and innovation program under grant agreement No 720743.



***Hermetia illucens* L.: A Source for Crude Fat for Industrial Use**

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The sustainable use of natural resources to produce raw materials based on renewable materials is the main goal worldwide. Beside plants- and mammal's oils and fats, producing fats from insects gained more and more interest in the last decades. The Hermetia Baruth GmbH is specialized on mass rearing of the Black Soldier Fly *Hermetia illucens* L..

The larvae of the Black Soldier Fly (BSF) are able to use nearly every organic waste to build up body mass. Under optimal development conditions the larvae of the last stage have a weight of up to 0.5 g. The percentage of crude protein in the dry mass is around 37%, the crude fat around 34%.



to

After a mechanical defatting process, the created meal has a protein content of around 58%. The most frequently amino acids in the protein are, Glutamine acid (ca. 3.9%), Asparagine acid (ca. 3.4%) and Leucin (ca. 2.6%). If registered feed is used for culturing BSF, from 1st of July within the EU, this protein is allowed to be used for feeding in aquaculture.



The compounds of the pure fat are 78 % saturated fatty acids and 21 % unsaturated fatty acids. The dominating fatty acid is lauric acid (46 up to 50 %), which is the most commonly used fat in the industrial production of soap.

According to EU law only registered feed for BSF can be used, if the fly is used for feeding animals. If this fly is used for producing amino acids and fatty acids for industrial use a lot of different waste materials can be taken into account.

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