abiosus e.V.
Non-Profit Association for the Advancement of Research on Renewable Raw Materials

7th Workshop on Fats and Oils as Renewable Feedstock for the Chemical Industry

March 23-25, 2014
Karlsruhe, Germany

in Cooperation with:
Karlsruhe Istitute of Technology (KIT)
German Society for Fat Science (DGF)
German Chemical Society (GDCh), Division of Sustainable Chemistry

KIT
Karlsruhe Institute of Technology

DGF
Deutsche Gesellschaft für Fettwissenschaft e.V.

Scientific and Organizing Committee

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Acknowledgement

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Program

Lectures and Posters

Sunday, March 23, 2014

Registration

Registration will be opened from 13:00 - 19:00

15.45	**Welcome and Opening**
	Ursula Biermann, *abiosus* e.V.
	Michael A. R. Meier, Division of Sustainable Chemistry of GDCh and KIT
16.00 – 17.45	*First Session* *Dedicated to Frank Gunstone on the occasion of his 90th birthday*
	Chair: Michael A. R. Meier
16.00 – 16.45	**Frank Gunstone – Teacher, Researcher, and Writer – A Celebration Lecture to Mark his 90th Birthday** (O)
L1	Marcel S.F. Lie Ken Jie, University of Hongkong, Hongkong, Peoples Republic of China
16.45 – 17.15	**Chemicals from Waste Bio-oils** (M)
L2	David Cole-Hamilton,[1] Ruben Duque Garcia,[1] Ronan le Goff,[1] Marc Furst,[1] Juma Mmongoyo,[2] James Mgaya,[2] Jennifer Julis,[1] Stuart Bartlett,[1] Sabrina Baader,[3] Quintino Mgani[2] [1]University of St. Andrews, St. Andrews,Scotland, UK; [2]University of Dar es Salaam, Dar es Salaam, Tanzania; [3] TU Kaiserslautern, Kaiserslautern, Germany
17.15 – 17.45	**Oleochemicals: Essential for Renewable Surfactants** (M)
L3	Dirk Leinweber, Clariant, Frankfurt, Germany
18.00 – 20.30	**Poster Session and Opening Mixer** Posters will be displayed until the end of the workshop

(O)	Opening Lecture 45 min
(M)	Main Lecture 30 min including discussion
(D)	Discussion Lecture 20 min including discussion

Monday, March 24, 2014

9.00 – 10.30 *First morning session*

Chair: David Cole-Hamilton

9.00 – 9.30 **Specialty Chemical Production from Natural Oils via Olefin Metathesis** (M)
L4 Stephen A. Cohen, Elevance Renewable Science, Woodridge, IL, USA

9.30 – 9.50 **Isomerizing Metathesis of Olefinic Substrates** (D)
L5 Sabrina Baader, Lukas J. Gooßen, Technische Universität Kaiserslautern, Kaiserslautern, Germany

9.50 – 10.10 **Renewable Polyamides and Polyesters by Straightforward Modification of Fatty Acid Methyl Esters and Efficient (Catalytic) Processes** (D)
L6 Matthias Winkler, M. A. R. Meier, KIT, Karlsruhe, Germany

10.10 – 10.30 **Branched Polyethylene Mimicry by Metathesis Copolymerization of Fatty Acid** (D)
L7 Etienne Grau, Bordeaux University – CNRS, France

10.30 – 11.00 **Coffee break**

11.00 – 12.50 *Second morning session*

Chair: Mats K. G. Johansson

11.00 – 11.30 **New General Purpose Plasticizers Made of Fatty Acid Derivatives** (M)
L8 Benjamin Woldt,[1] Andreas Gevers,[1] Michael Graß,[1] Stefan Buchholz,[1] Lucas Monteiro de Espinosa,[2] Michael Meier[2]
[1]Evonik Industries AG, Marl, Germany;[2] Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany

11.30 – 11.50 **Chemicals from Cashew Nut Shell Oil** (M)
L9 Stuart A. Bartlett, Jenny Julis, Juma Mmongoyo, David Cole-Hamilton, University of St. Andrews, St. Andrews, UK

11.50 – 12.10 **New Epoxy Materials from Cashew Nut Shell Liquid (CNSL)** (D)
L10 Emilie Darroman, Fanny Jaillet, Amédée Ratsimihety, Nelly Durand, Rémi Auvergne, Sylvain Caillol, Bernard Boutevin, Laboratory IAM ENSCM, Montpellier, France

12.10 – 12.30	**Synthesis and Characterization of Novel Vinylester Resins from Cardanol** (D)
L11	Fanny Jaillet, Sylvain Caillol, Hélène Nouailhas, Rémi Auvergne, Bernard Boutevin, Laboratory IAM ENSCM, Montpellier, France
12.30 – 12.50	**Biobased Aqueous Polyurethane Dispersions: A Case Study.** (D)
L12	Suresh Kattimuttathu Ittara, CSIR-Indian Institute of Chemical Technology, Hyderabad, India
12.50 – 14.00	**Lunch break**
14.00 – 15.30	*First afternoon session*
	Chair: Erik Heeres
14.00 – 14.30	**Vegetable Oil Chemical Valorization: Alkylation and Arylation of Glycerol** (M)
L13	Marc Lemaire, Université Claude Bernard Lyon 1, Lyon, France
14.30 – 14.50	**Nucleophilic substitutions and additions at unsaturated FAMEs.- An Access to fatty acid–conjugates** (D)
L14	H. J. Schäfer, M. Zobel, R. Maletz, L. Hinkamp, M. Plate, G. Feldmann, Westfälische Wilhelms-Universität, Organisch-Chemisches Institut, Münster, Germany
14.50 – 15.10	**Skeletal Isomerisation of Oleic Acid over Ferrierite** (D)
L15	Sophie C. C. Wiedemann,[1] Joseph A. Stewart,[1] Fouad Souliman,[1] Tanja van Bergen-Brenkman,[2] Stephan Langelaar,[2] Bas Wels,[2] Peter de Peinder,[1] Pieter C. A. Bruijnincx,[1] Bert M Weckhuysen,[1] [1] Utrecht University, Utrecht, Netherlands; [2] Croda Nederland BV, Netherlands
15.10 – 15.30	**Organic Carbonates and Renewable Resources: A Promising Alliance for the Sustainable Synthesis of Monomers and Polymers** (D)
L16	Oliver Kreye, Michael A. R. Meier, KIT, Karlsruhe, Germany
15.30 – 16.00	**Coffee break**

16.00 – 17.20 *Second afternoon session*

Chair: Filip du Prez

16.00 – 16.30 **Vegetable Oils for Wood Protection - Chemical Interactions with Wood Materials** (M)
L17 Mats K. G. Johansson, KHT, Stockholm, Sweden

16.30 – 17.00 **Hydrocarbon-Rich Biomass-Derived Thermoplastics, Thermoplastic Elastomers and Biomaterials** (M)
L18 Chuanbing Tang, University of South Carolina, Columbia, USA

17.00 – 17.20 **Structure-Property Relationships of Anhydride-cured Epoxidized Sucrose Soyate Thermosets: The Effect of Composition Variables (D)**
L19 Adlina Paramarta, Dean C. Webster, Department of Coatings and Polymeric Materials, North Dakota State University, Fargo ND, USA

19.30 *Conference Dinner*

Renaissance Karlsruhe Hotel

Tuesday, March 25, 2014

9.00 – 10.40	*First morning session*
	Chair: Chuanbing Tang
9.00 – 9.30 L20	**Biobased Polyamide Structures from Thiolacton Building Blocks** (M) Filip du Prez, University of Gent, Gent, Belgium
9.30 – 9.50 L21	**MacroRAFT Agents from Renewable Resources and their Use as Polymeric Scaffolds in a Grafting from Approach** (D) Sanne De Smet, Sophie Lingier, Filip du Prez, University of Gent, Gent, Belgium
9.50 – 10.10 L22	**From Fatty Acid Derived Polymers toward Polyethylene – Thermal Behavior of Polyesters, Polycarbonates and Polyacetals** (D) Patrick Ortmann, Stefan Mecking, Department of Chemistry, University of Konstanz, Konstanz, Germany
10.10 – 10.30 L23	**Novel Biobased Nonisocyanate Polyurethanes from Dimer Diamines Obtained from Solvent and Catalyst-free Synthesis: Study of the Structure-Properties Relationships (D)** Camille Carré**,** Luc Averous, ICPEES-ECPM, University of Strasbourg, Strasbourg, France
10.30 – 11.00	**Coffee Break**
11.00 – 12.50	*Second morning session*
	Chair: Ursula Biermann
11.00 – 11.30 L24	**Microbial Single Cell Oils - State of the Art and Challenges** (M) Christoph Syldatk, KIT, Karlsruhe, Germany
11.30 – 11.50 L25	**Microbial Oil as a Renewable Feedstock: Improving Single Cell Oil Properties by Metabolic Engineering** (D) Rodrigo Ledesma-Amaro, Universidad de Salamanca, Salamanca, Spain

11.50 – 12.10 **Synthesis of Aliphatic α-Branched Aldehydes *via* Combination of a Chemocatalytic Aldol Condensation and an Enzymatic C=C Reduction** (D)
L26 Marc Biermann,[1] Werner Hummel,[2] Harald Gröger[1]
[1] University of Bielefeld, Bielefeld, Germany; [2] University of Düsseldorf, Düsseldorf, Germany

12.10 – 12.30 **Large-ring Lactones from Fatty Acids** (D)
L27 Timo Witt, Philipp Roesle, Florian Stempfle, Josefine T. Christl, Hanna Busch, Gerhard Müller, Stefan Mecking, Department of Chemistry, University of Konstanz, Konstanz, Germany

12.30 – 12.50 **Esters of Oligo-(Glycerol Carbonate-Glycerol Ether) as Alternative to Fossil Surfactants** (D)
L28 Romain Valentin, Sébastien Holmière, Zéphirin Mouloungui,
Unité de Chimie Agro-Industrielle, UMR1010 INRA/INP-ENSIACET, Toulouse Cedex 4, France

12.50 – 14.00 **Lunch break**

14.00 – 16.00 *Afternoon session*

Chair: Dirk Leinweber

14.00 – 14.30 **Biodiesel Synthesis Using Centrifugal Contactor-separators: an Example of Process Intensification** (D)
L29 M.Y. Abduh,[1,2] A.Fernández-Martinez,[1] A. Kloekhorst,[1], H.J. Heeres,[1]
[1]University of Groningen, Groningen, The Netherlands; [2] Institut Teknologi Bandung, Bandung, Indonesia

14.30 – 14.50 **Oxidation Stability of *Jatropha curcas* Biodiesel Produced from High Free Fatty Acid Oil** (M)
L30 Supriyono Supriyono, Joana Maia Moreira Dias,
LEPABE, Department of Metallurgic and Materials Engineering, FEUP, Porto, Portugal

14.50 – 15.10 **Alkenolysis as a Path to Alternative Diesel Fuels Based on Methyl Oleate** (M)
L31 Marc R. L. Furst,[1] Friedrich Erben,[1] Daniel R. Riemer,[1] Benjamin Stengel,[2] Silvia Berndt,[2] Ulrike Schümann,[2] Evelyn Flügge,[2] Volker Wichmann,[2] Eckhard Paetzold,[1] Udo Kragl[3]
[1] Leibniz Institute for Catalysis at the University of Rostock; [2] Institute of Piston Machines and Internal Combustion Engines at the University of Rostock; [3]Institute for Chemistry, Division of Analytical and Technical Chemistry at the University of Rostock, Rostock, Germany

15.10 – 15.30 **Ethylene Production from Fats and Oils** (D)
L32 David Kubička, Jan Horáček, VUANCH, Litvínov, Czech Republic

15.30 **Poster Award and Closing Remarks**

Best Poster Award
Award committee: Marc Lemaire, Christoph Syldatk, Marcel Lie Ken Jie

Closing remarks
Michael A. R. Meier

16.00 **End of Workshop**

Posters

P1 **Acetalisation of glycerol to value added chemicals**
ALI M ALSALME,[1] Abdulaziz Alghamdi,[1] N Shiju[2] ; [1]King Saud University, RIYADH, Saudi Arabia; [2] University of Amsterdam, Netherlands

P2 **Photopolymerizable Synthons from Fatty acids and Glycerol Derivatives**
Ali MHANNA,[1] Faten SADAKA,[1] Gilles BONI,[1] Claire-Hélène BRACHAIS,[1] Laurent BRACHAIS,[1] Sylvie POURCHET,[1] Jean-Pierre COUVERCELLE,[1] Laurent PLASSERAUD,[1] Laurence LECAMP[2] ; [1] Institut de Chimie Moléculaire de l'Université de Bourgogne, Dijon, France ; [2] Normandie Université, INSA de Rouen, Rouen, France

P3 **Highly efficient grafting-onto Castor Oil derived Polymers using a Convertible Isocyanide**
Carsten Trefzger, Oliver Kreye, Michael A. R. Meier, KIT, Karlsruhe, Germany

P4 **Atom-efficient approaches towards diverse substituted polyamides applying the Ugi four-component reaction**
Patrick-Kurt Dannecker, Ansgar Sehlinger, Michael A. R. Meier, KIT, Karlsruhe, Germany

P5 **Renewable polyamides and polyureas derived from plant oils**
David E. Marschner, Oliver Kreye, Michael A. R. Meier, KIT, Karlsruhe, Germany

P6 **Divergent Dendrimer Synthesis via the Passerini three Component Reaction and Olefin Cross-Metathesis**
Dennis Kugele, Michael Meier, Oliver Kreye, Lorenz Faust, KIT, Karlsruhe, Germany

P7 **A two-step synthesis of dicarboxylic acids from homoallylic fatty derivatives using a ruthenium catalyst and H_2 acceptors**
Silvia Lopez-Chinarro, Mercè Balcells, Jordi Eras, Ruben Torregrosa, Xavier Hijós, Ramon Canela-Garayoa, Universitat de Lleida, Lleida (Spain)

P8 **Triazolinediones as a versatile click chemistry platform providing functionalization and cross-linking of plant oils**
Stijn Billiet, Oğuz Türünç, Johan Winne, Filip E Du Prez, University of Gent, Gent, Belgium

P9 **Easy synthesis of polyolesters with solid acid catalysts**
Matteo Mariani, Paolo Bondioli, Simona Brini, Rinaldo Psaro, Nicoletta Ravasio, Federica Zaccheria, STM-CNR, Università degli Studi di Milano, Milano, Italy

P10 **Catalyst Structure-Productivity and Structure-Selectivity Relationship in the Isomerizing Methoxycarbonylation of HO-Sunflower Oil**
Josefine Theresa Christl, Philipp Roesle, Florian Stempfle, Inigo Göttker-Schnetmann, Gerhard Müller, Stefan Mecking, University of Konstanz, Konstanz, Germany

11 **Plant-oil based linear long-chain aliphatic polyesters for injection moulding, film extrusion and electrospinning**
Florian Stempfle,[1] Benjamin Ritter,[2] Philipp Roesle,[1] Rolf Mühlhaupt,[2] Stefan Mecking[1]; [1] University of Konstanz, Konstanz, Germany; [2] Freiburg Research Center and Institute for Macromolecular Chemistry, Freiburg, Germany

P12 **Synthesis of renewable segmented polymer structures**
Sophie Lingier, Sanne De Smet, Filip Du Prez, University of Gent, Gent, Belgium

P13 **Lipase catalyzed synthesis of emollient esters in deep eutectic solvents**
Beatrice Kleiner, Ulrich Schörken, Fachhochschule Köln, Leverkusen, Germany

P14 **Terpene based polyesters via isomerizing methoxycarbonylation**
Hanna Busch, Stefan Mecking, University of Konstanz, Konstanz, Germany

P15 **Oils and Free fatty acids for the synthesis of biosurfactant mannosylerythritol lipids by Pseudozyma Species**
Susanne Zibek, Thomas Hirth, Steffen Rupp, Paula A Carrillo, Fraunhofer-Institut für Grenzflächen- und Bioverfahrenstechnik IGB, Stuttgart, Germany

P16 **Synthesis, characterization and electronic application of poly (linoleic acid)-g-poly(methyl methacrylate) graft copolymer**
Muharrem Gökçen,[1] Hayat Çulcu,[1] Sema Allı,[2] Songül Taran,[1] Mustafa Yasan,[1] Abdulkadir Allı[1]; [1]Düzce University, Düzce, TURKEY; [2] Bülent Ecevit University, Zonguldak, TURKEY

P17 **Illumination effect on electrical characterization of Au/poly (linoleic acid)-g-poly(methyl methacrylate) (PLiMMA)/n-Si diode**
Muharrem Gökçen,[1] Mustafa Yasan,[1] Abdulkadir Allı[1], Ahmet Demir,[1] Hayat Çulcu,[1] Sema Allı,[2]; [1]Düzce University, Düzce, TURKEY; [2] Bülent Ecevit University, Zonguldak, TURKEY

P18 **Synthesis and Characterization of New Poly(linoleic acid) Graft Copolymers**
Abdulkadir Allı,[1] Sema Allı,[2] Numan Uzun,[1] Muharrem Gökçen,[1] Baki Hazer[2]; [1]Düzce University, Düzce, TURKEY; [2] Bülent Ecevit University, Zonguldak, TURKEY

P19 **Hydroxylation of Oil/Oily Acid Peroxides for Synthesis of Graft Copolymers**
Abdulkadir Allı[1], Pınar Geçit[1], Sema Allı[2], Baki Hazer[2],
[1]Düzce University, Düzce, TURKEY; [2] Bülent Ecevit University, Zonguldak, TURKEY

P20 **Synthesis and Characterization of New Polyesters Containing Pendent Pentadecyl Chains**
Bhausaheb V. Tawade, Prakash P. Wadgaonkar, National Chemical Laboratory, Pune, India

P21 **Synthesis, properties and combustion behaviour of alternative diesel fuels originating from renewable resources**
Friedrich Erben,[1] Marc R.L. Furst,[1] Benjamin Stengel,[2] Daniel R. Riemer,[1] Silvia Berndt,[2] Ulrike Schümann,[2] Evelyn Flügge,[2] Volker Wichmann,[2] Eckhard Paetzold,[1] Udo Kragl[3]; [1] Leibniz Institute for Catalysis at the University of Rostock; [2] Institute of Piston Machines and Internal Combustion Engines at the University of Rostock; [3]Institute for Chemistry, Division of Analytical and Technical Chemistry at the University of Rostock, Rostock, Germany

P22 **Cyanoethylation of glycerol**
Frédéric Nadeu, Michèle Indt, Nicolas Oget, University of Lorraine, Metz, France

P23 **Novel techniques to optically characterize melt crystallization kinetics of high oleic sunflower oil based fatty acid mixture**
Sunanda Dasgupta, Karl Andreas Eckert, Peter Ay, Brandenburg University of Technology, Cottbus-Senftenberg, Germany

P24 **1,2,4-Triazoline-3,5-dione (TAD) chemistry for post-functionalization of the unsaturated renewable polymers**
Stijn Billiet, Oguz Türünc, Samira Ouardad, Kevin De Bruycker, Filip Du Prez, University of Gent, Gent, Belgium

P25 **Oleochemistry at KU Leuven: a catalytic view**
Joost Van Aelst, An Philippaerts, Pierre Jacobs, Bert Sels, Centre for Surface Chemistry and Catalysis, Heverlee, Belgium

P26 **Novel terpene based bifunctional monomers for biopolymer production**
Irina Funk, Michael Hofer, Volker Sieber, Lehrstuhl für Chemie Biogener Rohstoffe, TU München, Straubing, Germany

P27 **Transition-Metal Catalyzed Polymerization of Novel Biogeneous Monomers**
André Fleckhaus, Gerd Klaassen, Helga Meyer, Paul Rakowski, Mark Rüsch gen. Klaas, University of Applied Sciences Emden-Leer, Emden, Germany

P28 $[Pd(\mu\text{-}Br)P(t\text{Bu})_3]_2$: A Highly Active Isomerization Catalyst for Unsaturated Compounds

Patrizia Mamone, Sabrina Baader, Dominik M. Ohlmann, Lukas J. Gooßen, Technische Universität Kaiserslautern, Kaiserslautern, Germany

P29 Process optimization of biotransformation based bifunctional monomer generation via Candida tropicalis

Nina Rimmel, Michael Hofer, Volker Sieber, Lehrstuhl für Chemie Biogener Rohstoffe, TU München, Straubing, Germany

P30 Polymerization of linseed oil via acyclic triene metathesis (ATMET)

Cristian O. Romera,[1] Priscilla B. Cardoso,[1,2] M.A.R. Meier,[2] Claudia Sayer,[1] Pedro H. H. Araújo[1]; [1]Federal University of Santa Catarina, Florianópolis, SC, Brazil; [2] Karlsruhe Institute of Technology, Karlsruhe, Germany

P31 ADMET and thiol-ene reactions in miniemulsion

Priscilla B. Cardoso,[1,2,3] Anna Musyanovych,[2] Katharina Landfester,[2] Claudia Sayer,[1] Pedro H. H. Araújo,[1] M.A.R. Meier[3]; [1] Federal University of Santa Catarina, Florianópolis, SC, Brazil; [2] Max Planck Institute for Polymer Research, Mainz, Germany, [3] Karlsruhe Institute of Technology, Karlsruhe, Germany

Abstracts

Part 1: Lectures

L1

Frank Gunstone – Teacher, Researcher, and Writer – A Celebration Lecture to Mark his 90th Birthday

Marcel S.F. Lie Ken Jie, University of Hongkong, Hongkong, Peoples Republic of China
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The presentation starts by taking the audience through the nostalgic postwar years of Organic Chemistry and highlights the pioneering work by Frank Gunstone in discovering a number of novel fatty acids (incl. isoricinoleic and vernolic acid) in seed oils. The impact of these discoveries provided Gunstone with fresh insights into the structures of natural fat molecules and prompted him to pursue new and challenging ideas in fatty acid research. He arrived at the University of St. Andrews in 1954 from Glasgow University, where he had taught Organic Chemistry and had studied the composition of seed oils for eight years. The 1960s and 70s in St. Andrews witnessed him break new grounds through his brilliant work on the reactions of unsaturated and oxygenated fatty acid molecules (with emphasis on neighboring group participation reactions) and on the total synthesis of several series of closely-related unsaturated and oxygenated fatty acids. The large range of diverse types of fatty acids (obtained from chemical reactions of natural fatty acids or through total synthesis) placed him in a unique position to study these series of closely-related fatty acids rigorously in a systematic manner using the emerging state-of-the-art analytical techniques (TLC, GC, NMR and MS). In the following decade (1980s) Gunstone continued unabated in his research, as the state-of-the-art techniques became more advanced. His synthesis work covered exotic fatty acid molecules containing heteroaromatic, sulphur and other chemical groups. Frank Gunstone's talent as a teacher and a writer is unsurpassed. His unreserved attitude to share his knowledge is demonstrated by the numerous textbooks in Organic Chemistry, specialist books on fatty acid chemistry, scientific publications (forming a collection of some 400 reviews, scientific papers and book publications). His expertise was tapped by industries and governments, local as well as from overseas. He served as the Chief Editor of the journal Lipid Technology for 20 years. The speaker is honored to reflect on the great works by a distinguished man with whom he has been associated with for half a century.

L2

Chemicals from Waste Bio-oils

David Cole-Hamilton,[1] Ruben Duque Garcia,[1] Ronan le Goff,[1] Marc Furst,[1] Juma Mmongoyo,[2] James Mgaya,[2] Jennifer Julis,[1] Stuart Bartlett,[1] Sabrina Baader,[3] Quintino Mgani[2]
[1]University of St. Andrews, St. Andrews,Scotland, UK; [2]University of Dar es Salaam, Dar es Salaam, Tanzania; [3] TU Kaiserslautern, Kaiserslautern, Germany
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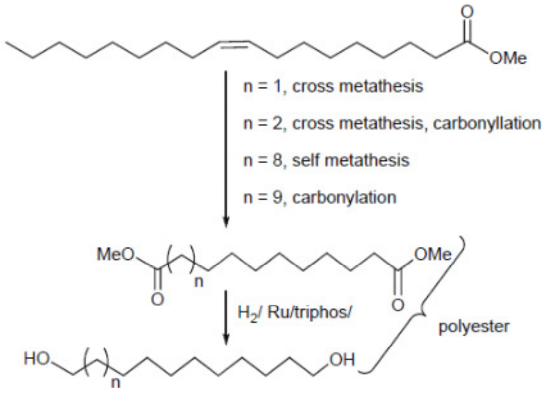
As oil supplies dwindle and the price increases, it is essential to find new ways of making the many chemicals on which the quality of our lives depends. One approach is to use renewable resources which can be grown. However, there is a tension between using land for fuel or chemicals production and the need to use land to produce food for the rapidly increasing world population. One possible solution is to use waste products for the manufacture of chemicals. In this presentation, we shall discuss the conversion of methyl oleate and oleic acid, a major component of *Tall Oil,* a waste from wood processing, into polymer precursors. We shall also discuss the synthesis of a range of important chemicals from cashew nut shell liquid (CNSL), a waste from cashew nut processing.



Scheme1. The formation of a range of α,ω–difunctionalised compounds from methyl oleate using homogeneous catalysis

We shall show how homogeneous carbonylation,[1] metathesis, and reductive amination[2] (see Scheme 1) can be used to make difunctional esters acids, alcohols and amines[1a, 3] for polymer formation[4] (Figure 1).

Since homogeneous catalysts suffer the potential difficulty of product-catalyst separation, we shall show how supported ionic liquid phase SILP) catalysts with carbon dioxide flow (see Figure 1) allow the ready separation of the products from the catalyst, thus overcoming one of the major difficulties associated with scaling up and using homogeneous catalysts commercially. We shall describe our developments on metathesis[5] and other reactions using these systems.

Cashew nut shell liquid contains interesting phenols *meta* substituted with an unsaturated C_{15} chain. We shall described how it can be used to synthesise tse-tse fly attractants, potentially safe detergents, polymer additives, monomers for polymerisation and large ring macrocyclic lactones.[6] (Figure 2.

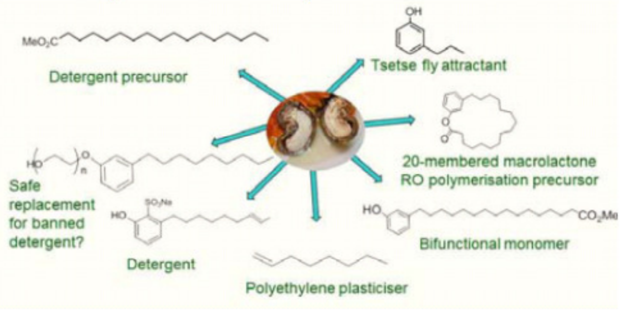


Fig. 2 Chemicals from cashew nut shell liquid

[1] a) C. Jimenez-Rodriguez, G. R. Eastham, D. J. Cole-Hamilton, *Inorg. Chem. Commun.* **2005**, *8*, 878; b) C. J. Rodriguez, D. F. Foster, G. R. Eastham, D. J. Cole-Hamilton, *Chem. Commun.* **2004**, 1720.
[2] A. A. Nunez Magro, G. R. Eastham, D. J. Cole-Hamilton, *Chem. Commun.* **2007**, 3154.
[3] a) M. R. L. Furst, R. le Goff, D. Quinzler, S. Mecking, D. J. Cole-Hamilton, *Green Chem.* **2011**, *14*, 472; b) M. R. L. Furst, T. Seidensticker, D. J. Cole-Hamilton, *Green Chem.* **2013**, *15*, 1218
[4] a) D. Quinzler, S. Mecking, *Angew. Chem. Int. Ed.* **2010**, *49*, 4306; b) F. Stempfle, D. Quinzler, I. Heckler, S. Mecking, *Macromol.* **2011**, *44*, 4159.
[5] R. Duque, E. Ochsner, H. Clavier, F. Caijo, S. P. Nolan, M. Mauduit, D. J. Cole-Hamilton, *Green Chem.* **2011**, *13*, 1187.
[6] J. A. Mmongoyo, Q. A. Mgani, J. M. Mdachi, P. J. Pogorzelec, D. J. Cole-Hamilton, *Eur. J. Lipid. Sci. Technol.* **2012**, *114*, 1183.

L3

Oleochemicals: Essential for Renewable Surfactants

Dirk Leinweber, Clariant, Frankfurt, Germany
Dirk.Leinweber@clariant.com

A great degree of importance is placed on sustainability in Clariant´s corporate strategy[1]. As a globally leading company in the field of specialty chemicals, Clariant puts strong emphasis on environmental protection and safety in all its activities. One approach, which is effectively applied by Clariant, is the use of sustainably sourced renewable feedstocks in the production of value-added chemicals by 1) production of specialty chemicals such as renewable surfactants from bio-based substrates and 2) transformation of agricultural waste into value-added building blocks suitable for further transformation into renewable surfactants.

Surfactants are among the highest volume synthetic chemicals produced globally[2,3]. For 2012 the global surfactants market is estimated to be about 29 billion US$ with a growth rate of about 6%. The large demand for surfactants calls for sustainable surfactants made from renewable raw materials in order to reduce environmental impact and save fossil fuel resources. The molecular structures of starting materials from renewable feedstocks such as amino acids, sugars, fatty acids and organic acids create new opportunities to obtain innovative value-added specialty chemicals. However, the success of newly developed bio-based products is obviously dependent on two major aspects: cost and performance. In order to achieve this, classical oleochemicals such as plant oils, fatty acids and fatty alcohols are used; they continue to be the building blocks of choice to develop novel renewable and cost-performing surfactants. A challenging task for industrial R&D work is to develop innovative surfactants based on natural building blocks with application properties that are comparable or superior to petrochemical surfactants, while maintaining a low production cost, in order to be able to introduce a new bio-based product successfully into the market.

In this presentation two specific examples of successful renewable surfactant launches based on oleochemicals are given: Synergen OS, a highly efficient adjuvant for Crop Protection, and Velsan SC, a synergistic preservative booster for Personal Care.

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L4

Specialty Chemical Production from Natural Oils via Olefin Metathesis

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Elevance employs olefin metathesis to produce high performance, cost-advantaged chemicals from renewable oils. The core catalyst technology is based on the work of Professor Robert H. Grubbs and the catalyst is used in a highly efficient process to produce olefins and novel fatty ester derivatives. In 2013, Elevance completed construction and began production at a world-scale metathesis biorefinery in Gresik, Indonesia. Also in 2013, Elevance commercialized the Inherent™ C18 diacid. Elevance's biorefinery process and biorefinery products will be discussed along with some of the market applications for the products.

L5

Isomerizing Metathesis of Olefinic Substrates

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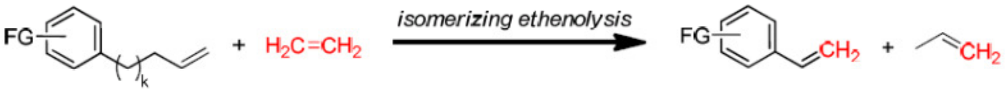
In the isomerizing olefin metathesis process, a bimetallic palladium / ruthenium system efficiently converts fatty acids into industrially useful multi-component blends.[1] Technical quality fatty acids can be employed in isomerizing self-metathesis, ethenolysis, or cross-metathesis reaction, leading to olefin blends of tailored medium chain lengths from renewable resources rather than from crude oil. The mono- and dicarboxylates formed as secondary products create additional value when used as polymer building blocks.

The same process can give access to styrenes when applied to alkenylbenzenes, which may also originate from renewable sources.[2] Initially, the isomerization catalyst generates a mixture of double-bond isomers, which are continuously converted into shorter olefins by ethenolysis, finally leading to the desired styrene.



A similar isomerizing butenolysis reaction can give access to the tsetse fly attractant 3-propylphenol when applied on Cardanol, a phenol with a long olefin side chain obtained from cashew nutshell liquid (*CNSL*).[3]

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L6

Renewable Polyamides and Polyesters by Straightforward Modification of Fatty Acid Methyl Esters and Efficient (Catalytic) Processes

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Polyamides from renewable resources are of great interest due to their lower environmental impact and their potential to substitute fossil based high-performance polymers. Herein, the olefin cross-metathesis of unsaturated fatty acid methyl ester (FAME) derived benzyl carbamates with methyl acrylate is presented. The corresponding FAME benzyl carbamates were prepared via a catalytic Lossen rearrangement utilizing dibenzyl carbonate and benzyl alcohol. Moreover, the catalytic oxidation of FAMEs with molecular oxygen as sole oxidant will be discussed for the synthesis of branched polyamide monomers.[1] The employed synthesis strategies have potential for the bio-sourced preparation of monomers for the production of diverse polyamides and polyesters. The different synthesis strategies will be introduced and the properties of the resulting polymers compared to each other.

L7

Branched Polyethylene Mimicry by Metathesis Copolymerization of Fatty Acid

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Despite the numerous applications of PE materials, the latter do not constitute a sustainable solution, in particular for environmental applications, as evidenced by their lack of hydrolytic degradability. With the aim to introduce potentially degradable segments to a PE backbone while keeping its characteristics, a lot of efforts have been carried out these last years to design sustainable and bio-based “polyethylene-like” polyesters. Most of the studies performed on the development of “PE-like” polyesters from fatty acids resulted in materials that mimic the structure of HDPE.

On the contrary, very few investigations were carried out to synthesize “LDPE-, LLDPE- and VLDPE-like” polyesters from plant oils. In this work, we develop new “LLDPE- and VLDPE-like” polyesters through ADMET copolymerization or polycondensation of fatty-acid based monomers. The thermo-mechanical properties of the so-formed polymers were investigated and compared to their petroleum-based analogues.

L8

New General Purpose Plasticizers Made of Fatty Acid Derivatives

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As a leading plasticizer producer in Europe Evonik is always looking for new plasticizer structures. General purpose plasticizers like VESTINOL® 9 or ELATUR® CH are utilized to produce soft PVC which is used for flooring, wallpapers, roofing, hoses for example. Phthalates are still the dominating plasticizer class worldwide. This is due to a good overall performance, low prices and high available volumes. Apart from these petrochemical standards the market share of phthalate free alternatives and biobased plasticizers is constantly increasing. An interesting group of plasticizer which is made of renewable feedstocks are modified fatty acid esters, which can be synthesized from plant oils, fatty acids or biodiesel.

New plasticizer structures using fatty acid derivatives as a feedstock were developed in cooperation with the KIT. Technically relevant plasticizers have been identified, structure modifications and process optimizations have been done and a broad set of application tests has been performed.

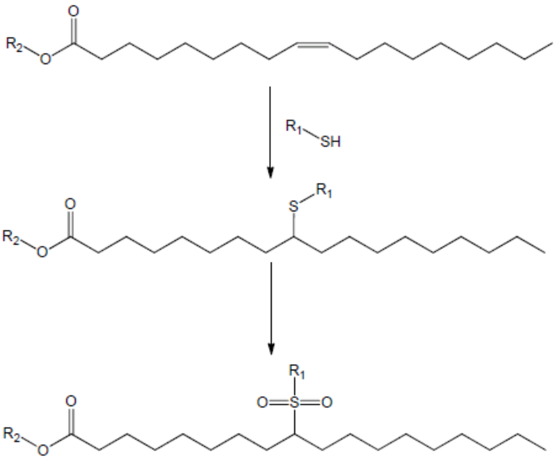

Figure 1: Synthesis of sulfone modified fatty acid esters.

The combination of thiols and fatty acid derivatives can result in a new class of plasticizers. Via a Thiol-ene addition a thioether can be introduced in the fatty acid chain. The thioether can be oxidized with hydrogen peroxide under mild conditions to get the corresponding sulfones. The formed plasticizers were used to produce different transparent PVC films. The application tests have shown that the sulfones have a balanced property profile with strengths in gelation behavior and plasticizer efficiency. With minor recipe adaptions sulfon modified fatty acid esters should be usable as general purpose plasticizers in flexible PVC.

L9

Chemicals from Cashew Nut Shell Oil

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Renewable and natural resources must be developed to replace oil based materials which are depleting at an alarming rate. Cashew nut shell liquid is a biodegradable and renewable natural resource, available as a by-product of the Cashew nut processing industry at around 600 000 t pa-1.[1] Solvent extraction gives mainly anarcardic acid, which on heating to 200 degrees C, loses CO2 to give predominantly cardanol.[2] Having a 15-carbon side chain meta to a phenolic group with varying unsaturation makes cardanol a potentially valuable substrate for chemical manipulation in the replacement of oil based resources.

By employing carbon-carbon double bond isomerisation and metathesis methodologies, cardanol has provided new routes towards several useful products in the manufacturing industry. These include detergents and detergent precursors by routes of metathesis and sulfonation, 1-octene (a olefin monomer) and 3-(non-8-enyl)phenol from the direct metathesis of cardanol with ethylene and also, a new three step route to a tsetse fly kairomone component (3-propylphenol).[3] Including a new range of phenolic polymers. This demonstrates the huge potential of phenolic compounds of cashew nut shell liquid in the drive for renewable resources.

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L10

New Epoxy Materials from Cashew Nut Shell Liquid (CNSL)

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The exhaustion of fossil fuels urges chemistry community to look for new raw materials coming from renewable resources in substitution to petrobased monomers. One of the most petrobased monomers used in epoxy materials is bisphenol A, which is a toxic aromatic compound that tends to be replaced. However, the availability of bio-based aromatic compounds is poor while the aromatic rings play a fundamental role in the structure of polymers. Indeed, they provide the thermal and mechanical properties required for some applications. There is to date only three sources providing access to biobased aromatic monomers: lignin, the most important, flavonoids and cardanol, still little known.

Cardanol is extracted from the oil of cashew nutshell liquid (CNSL), this oil is commercially available with a global production of 450 000 tons per year. Commercial epoxidized cardanol, synthesized from cardanol, is a reactive biobased aromatic epoxide reactant with an interesting structure. The epoxidized cardanol was carefully analyzed by 1H and 13C NMR, by steric exclusion chromatography, and by titration to determine its structure and functionality.

Several formulations were performed with various diamines to synthesize epoxy networks. In order to optimize the properties of the materials based on epoxidized cardanol, new biobased epoxide compounds were added in various amounts. Thus, the thermal and mechanical properties could be modulated with sugar derivatives such as sorbitol polyglycidyl ether or isosorbide polyglycidyl ether.

These epoxy systems have been characterized mechanically and thermally, and then they were compared with the ones formulated with the diglycidyl ether of bisphenol A (DGEBA). Hardness and brightness tests have been done to evaluate the properties of these new biobased materials as coatings, as well as tests of resistance to acids and alkalis. The materials obtained from the epoxidized cardanol exhibit interesting mechanical and thermal properties, and can be used as coating materials or binders for composite materials.

L11

Synthesis and Characterization of Novel Vinylester Resins from Cardanol

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In order to reduce the use of petrochemical derived monomers in housing applications and to use bio-based raw materials, a novel thermosetting vinylester (VE) resin was prepared from cardanol. Cardanol is extracted from Cashew Nut Shell Liquid (CNSL), a non-edible renewable resource by-product from the cashew industry. This vinylester resin was developed to be used as a matrix in composite materials for window frames shaped by pultrusion process.

Cardanol has an interesting aromatic structure and constitutes a good natural alternative to petro chemically derived phenols. Cardanol-based VE prepolymers were synthesized by the reaction between epoxidized cardanol commercialized by Cardolite and methacrylic acid. The chain-end insaturation allowed curing by radical polymerization with a copolymerizable monomer, also called reactive diluent. Even though styrene remains the most widely used reactive diluent in vinylester resins, this monomer is known to be very volatile and to be harmful. Consequently, new monomers such as isobornyl methacrylate (IBOMA), dibutyl itaconate (DBITA), butanediol dimethacrylate (BDDMA) and hexanediol dimethacrylate (HDDMA) were selected as styrene substituents, because they are less volatile and less harmful. Materials were prepared from the cardanol-based VE prepolymer and from these five reactive diluents, i.e. styrene, IBOMA, DBITA, BDDMA, HDDMA. On the other hand, materials were also prepared from bisphenol A diglycidyl ether (BADGE)-based VE prepolymer and styrene as reactive diluent in order to compare the properties of all materials. Thermal and mechanical properties were measured in order to compare materials for the selected application.

L12

Biobased Aqueous Polyurethane Dispersions: A Case Study

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Global approaches to sustainable development are aimed at utilization of renewable resources in fine chemical manufacturing. Unlike the petroleum feedstocks, the number of renewable resources that can serve as potential feedstock for chemicals is varied in composition and origin and thus there is felt need for detailed structure–property correlation studies to understand and improve the potential of these resources fully. Cashew nut shell liquid (CNSL), a renewable resource obtained as a by product of the cashew industry has been utilized in industrial applications for ages. The unique structural characteristics of CNSL offer plenty of opportunities to fine tune the properties with novel applications. Among bio-based chemicals, development of polyols for polyurethanes from renewable resources have attracted much interest from academic and industrial laboratories.[1,2] The utilization of these natural polyols in the synthesis of aqueous polyurethane dispersions has increased substantially in recent years.[3] In this work we present a case study with a renewable resource based on cardanol, the main constituent of CNSL, in the preparation of aqueous PU dispersions. The impact of the polyol structure on synthesis, film formation and film properties will be highlighted. Comparison is made between polyols based on the widely used triglyceride oils and the cardanol polyol.

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L13

Vegetable Oil Chemical Valorization: Alkylation and Arylation of Glycerol

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“Biodiesel”, i.e. fatty acid methyl esters, has been widely implemented in the EU and the US since it has proved to be a valuable fuel for diesel engines, being both renewable and clean. It is obtained from vegetable oils (soybean, rapeseed …) by a transesterification process with alcohols. The sharp rise in world biodiesel production has created a glut of glycerol, which is a by-product of the transesterification process. Today, its production is estimated to 2.6 million metric tons against 1.0 million metric tons in 2005 thus resulting in lower prices for this raw material. Therefore, the sustainability of this branch requires the development of new markets. In our laboratory, we have been interested in the synthesis of glycerol derivatives, especially of non-symmetrical 1-O-alkyl glycerol ethers. These compounds are amphiphilic molecules used as performance additives in various industrial fields (textiles, leather, metallurgy ...) and are also present in the formulations of end-user products such as detergents, cosmetics, industrial cleaning... Non-symmetrical 1-O-alkyl glycerol ethers belong to the family of non-ionic surfactants that are very popular because of their low irritancy and their high stability in acidic medium. Traditionally, these ethers are prepared via the Williamson ether synthesis, despite the need for a strong base and the generation of stoechiometric amounts of saline waste. Moreover, the few procedures that are reported in the literature for the synthesis of ethers implementing catalysts (nickel on silica, platinum oxide, acid catalysis ...), give only low yields.
More than 15 years ago, our group discovered an alternative method to the Williamson etherification of carbonyl compounds with primary or secondary alcohols using Pd/C as a catalyst under hydrogen pressure. This method allows the synthesis of ethers with high yields and generates water as the sole by-product. However, to the best of our knowledge, this method has never been applied to polyols in mild conditions. The few examples reported are patents that describe two step-procedures, at high pressures and temperatures. This long-underexploited reaction was recently trendy with the increased interest for glycerol chemistry that allowed us to find a real application in cooperation with a major industry in the French sector of vegetable oils / proteins and a leader company in specialty chemicals. The application of this reaction to glycerol was realized through the use of Pd/C, H_2 pressure, and a Brønsted acid as a co-catalyst. Under optimized conditions, the reaction of an aldehyde or a ketone with glycerol afforded the corresponding 1-O-alkyl glycerol ethers with both high yields and selectivity. Same products can also be obtained from carboxylic acid and glycerol. These two methodologies have also been extended to larger polyols such as diglycerol. In addition, aryl ethers of glycerol could also be obtained using another new technology: the dehydrogenative alkylation. Finally using Phase transfer catalysis, the trimethoxy propane was synthesized in high yield starting from glycerol this new solvent had useful physical and chemical properties and low toxicity.

M. Lemaire related publications: Green Chemistry (2013), 15(11), 3020-3026; ACS Sustainable Chemistry & Engineering (2013), 1(11), 1463-1473; European Journal of Organic Chemistry (2013), 2013(26), 5902 5916; ChemCatChem (2013), 5(10), 2893-2904; European Journal of Organic Chemistry (2013), 2013(24), 5445-5454; Journal of Physical Chemistry B (2013), 117(31), 9262-9272; Green Chemistry (2013), 15(3), 786-797; Green Chemistry (2013), 15(2), 347-352; Catalysis Communications (2012), 29, 58-62; ChemSusChem (2012), 5(12), 2397-2409; Green Chemistry (2011), 13(10), 2737-2742; Green Chemistry (2010), 12(12), 2189-2195; Science China: Chemistry (2010), 53(9), 1953-1956; Tetrahedron Letters (2009), 50(49), 6891-6893; Tetrahedron Letters (1995), 36(24), 4235-6.

L14

Nucleophilic substitutions and additions at unsaturated FAMEs.- An Access to fatty acid–conjugates

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Nucleophiles can be connected with unsaturated FAMEs by epoxidation and ring opening of the epoxide with a nucleophile.

Alternative routes are the nucleophilic addition at an activated double bond, the electrochemical oxidative addition of a nucleophile at a double bond, and the nucleophilic substitution of a leaving group.

A double bond can be activated for a nucleophilic addition by conjugation to the electron attracting carbonyl group. This is achieved by oxidation of the hydroxy group in methyl ricinoleate to a keto group and a subsequent conjugation of the double bond. At the activated double bond of the enone carbon–, oxygen– and nitrogen–nucleophiles as malonates, cyanide enolethers, nitroalkanes, alcohols and amines were added as shown in examples.[1]

By anodic “Umpolung” the nucleophilic diene in conjugated methyl linolenoate can be converted into an electrophilic radical cation that reacts with nucleophiles as alcohols and acetic acid to 1,4-diethers and 1,4-diols of methyl octadecenoate.[2]

Allylic hydroxylation for performing a substitution at the fatty acid chain was achieved by photooxidation with singlet oxygen or a SeO_2/*t*-BuOOH oxidation. Nucleophiles can then be introduced by palladium(0)-catalysis or with DEAD/Ph_3P.[3]

These reactions enable conversions to higher value oleochemicals. Furthermore they allow a quick access to fatty acid–conjugates, where a bioactive compound or a material with useful physical properties is covalently attached to the alkyl chain of a fatty acid. This combination allows enriching the active compound in micelles, vesicles and at interphases and facilitating the transport through membranes. Preparations of fatty acid–conjugates with carbohydrates, steroids, an azo dye[4], heterocycles[4] and phenols and will be presented.

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L15

Skeletal Isomerisation of Oleic Acid over Ferrierite

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Branched-chain fatty acids (bc-fas) are used extensively in the production of e.g. lubricants, cosmetics and surfactants, for which liquidity, good thermal and oxidative stability and useful interfacial properties are highly valued. The current commercial process for making bc-fas from oleic acid uses a montmorillonite clay as catalyst [1]; yields are 50% or less, the balance being predominantly polymerised acids. Zeolites are promising alternative catalysts for a more efficient synthesis of bc-fas and have been investigated by several research groups. Recently, improvements in both conversion and selectivity were reported using a commercial ferrierite, and selectivity was further enhanced by the addition of a Lewis base [2]. However, re-use was reported to be possible only after a costly regeneration step [3].

We have carried out a comprehensive study of the catalytic performance and deactivation of ferrierite during the skeletal isomerisation of oleic acid, in order to improve stability of the present catalytic system and to propose an optimum regeneration strategy. UV-Vis and FT-IR spectroscopic analyses of the spent catalyst materials, complemented by NMR and mass spectrometry of the coke deposits extracted after HF dissolution, has provided new insights into the deactivation mechanism at hand.

The high initial catalyst activity and selectivity are quickly lost, despite conservation of the framework integrity, as a result of severe deactivation. Pore blockage is detected very early on in the reaction, and only the pore mouth of the zeolite material is actively employed. Additionally, polyenylic carbocations, which are formed by hydrogen transfer reactions, poison the active sites; they are considered to be the precursors to traces of condensed aromatics detected in the spent catalyst. Furthermore, dodecyl benzene is the major “coke” constituent, and its precursor is believed to compete for the active sites.

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L16

Organic Carbonates and Renewable Resources: A Promising Alliance for the Sustainable Synthesis of Monomers and Polymers

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Organic carbonates, especially dimethyl carbonate, offer manifold possibilities for green chemistry, ranging from a possible substitution of phosgene to sustainable alkylation reactions.[1]

Recently, organic carbonates were shown to be excellent activation reagents for hydroxamic acids to initiate a base catalyzed Lossen rearrangement to obtain alkyl carbamates.[2]. Applying this approach, fatty acid derived dialkyl carbamates were obtained, which are key compounds for the synthesis of novel phosgene- and isocyanate-free polyurethanes as well as for renewable polyamides.[3],[4] Furthermore, studies on esterifications and alkylations of phenolic acids (also from renewable sources) revealed that selective esterification in the presence of phenolic-OH groups are possible.[5] Moreover, the conversion of phenolic acids with ethylene carbonate gave valuable monomers for the synthesis of renewable copolymers.[6]

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L17

Vegetable Oils for Wood Protection - Chemical Interactions with Wood Materials

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Vegetable oils and derivatives thereof have a long tradition in the field of organic coatings [1]. Oil based resins are dried via chemical crosslinking reactions that either are oxidation reactions using atmospheric oxygen (alkyds or linseed oil coatings) or other chemical reactions such as cationic polymerization (epoxidized oils) and amino crosslinking reactions (alkyd / melamines). Systems based on polyunsaturated fatty acids normally dry via an oxidative crosslinking route catalyzed by various driers such as transition metals salts[2]. These systems range from linseed oil paints to more modern alkyd based systems and hybrid systems such as alkyd/acrylates. The coating applications range from impregnating oils on wood where the oils act as a primer that hydrofphobize the wood surface to alkyd top coats for both wood and metal substrates. The widespread use of vegetable oil monomers in a large variety of coatings indicates that these monomers have intrinsic properties suitable for protective coatings. The use of vegetable oil based monomers has however not increased too much during the 1900´s due to competition from synthetic monomers such as acrylates and other fossil based raw materials. Increased environmental concerns in combination with increased oil prices and development of new chemistries as well as modern crops development has however spurred an increased interest both academically as well as industrially for monomers based on renewable resources [3]. One area were vegetable oils have kept a strong position is as primers for wood substrates were the function of the primer is to modify the hydrophilic wood material surface to become more hydrophobic. The primer should furthermore provide good adhesion to the top-coating and be durable as durable as possible. It has also been shown in numerous studies that vegetable oils have a positive effect on the exterior durability of the wood during weathering [4]. The oxidative drying of vegetable oils has been extensively studied in order to reveal the drying mechanism [2]. It has been shown that the drying proceed via an auto-oxidation mechanism where the bis allylic protons in an polyunsaturated fatty acid is abstracted by an peroxy radical to form an hydroperoxide and a carbon centered radical. The formed carbon centered radical then rapidly reacts with atmospheric oxygen to form a new peroxy radical that abstracts the next bis-allylic proton and so on. The formed hydroperoxides then decompose to form alkoxy radicals that contribute to crosslinking via coupling reactions and the oil then dries. A vast majority of the studies have been performed as model studies on either in bulk or on inert substrates with a focus on the drying mechanism. Less has been done in studying this drying mechanism when combined with an active substrate such as wood. Studies have rather focused on the effect of oils on the performance of the final material than the actual drying of the oil. Some studies utilizing chemiluminescence however indicate that wood substrates do interact with wood during the drying and this implies that not only the intrinsic reactivity of the oil is important but also how these reactions are affected by the presence of wood [5].

The present study gives an overview of findings on how oxidatively drying oils interact with wood during the drying reactions using FTIR and NMR techniques [6,7,8,9]. Both studies on combination of oils and different wood constituents as well as different wood varieties will be described. The results strongly suggest that the choice of oil will have a significant effect on the system performances.

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L18

Hydrocarbon-Rich Biomass-Derived Thermoplastics, Thermoplastic Elastomers and Biomaterials

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Over the past two decades the polymer science field has observed an explosive growth of controlled macromolecular engineering for precision synthesis of structural details and complexities of macromolecules toward function-driven applications. We have adopted macromolecular engineering in conceptualizing and developing research projects that target on functional building blocks from natural resources to design novel polymeric architectures. The synthetic methodology encompasses from the derivatization of molecular biomass to controlled polymerization. This presentation will be focused on the development of renewable polymers from a class of hydrocarbon-rich biomass by tuning macromolecular architectures. While synthesis of engineering polymers from simple thermoplastics to thermoplastic elastomers to biocomposites aims for sustainable materials, we will also demonstrate how to utilize the unique structure and function of hydrophobic natural moiety to develop novel antimicrobial biomaterials.

L19

Structure-Property Relationships of Anhydride-cured Epoxidized Sucrose Soyate Thermosets: The Effect of Composition Variables

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Epoxidized sucrose soyate is a novel bio-based epoxy resin derived from sucrose and soybean oil fatty acids, and it contains up to 12 epoxy functional groups per molecule. This epoxy resin was crosslinked with a cycloaliphatic anhydride, i.e. methyl hexahydrophthalic anhydride, to form polyester thermosets with high crosslink density; the epoxy-anhydride reaction was catalyzed using a zinc-complex catalyst. In this work, we examined the structure-property relationships of the thermosets by varying key composition variables: the anhydride-to-epoxy molar ratio and catalyst amount. These variations are expected to influence the chemical, mechanical and thermal properties of the thermosets. We investigated the network formation through soxhlet extraction, which provides the amount of insoluble material and the composition of the soluble materials. Then, the mechanical properties were studied through tensile testing, which provides the Young's modulus, tensile strength and elongation at break. Finally, we assessed the thermal properties through dynamic mechanical analysis (DMA), which provides us the thermosets' glass transition temperatures and crosslink densities. The results provide insight into the molecular network structure of the thermosets and the range of properties that can be obtained as a function of the composition variables.

L20

Biobased Polyamide Structures from Thiolacton Building Blocks

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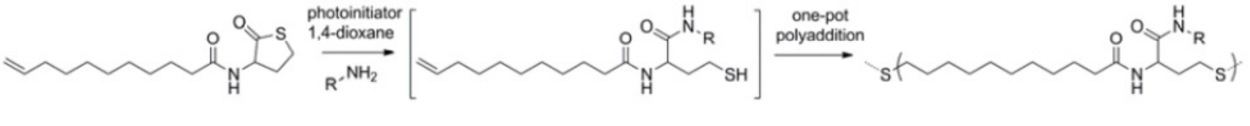
In recent years, the interest in polymer modification reactions involving thiols has much increased. Our research interest consists of the exploration of the reactivity of a thiolactone unit as a latent thiol functionality. *N*-acetylhomocysteine thiolactone, readily available in large scale from renewable resources, was already used for the introduction of thiol groups in natural proteins, through the nucleophilic ring-opening by the ε-NH_2 groups of lysine residues. We adapted this method and combined it with both radical and nucleophilic thiol-ene reactions for the synthesis of polymeric materials, starting from stable amino compounds. Indeed, a thiolactone should be considered as a protecting group for a thiol, allowing us to avoid possible unwanted disulfide formation and the use of smelly thiols, whilst in the meantime introducing many types of functionalities through the choice of the amine. This amine-thiol-ene conjugation is considered to be a quite relevant extension to the currently existing thiol-ene chemistries, allowing for a one-pot synthesis of various functionalized polymeric materials.[1-3]

Recent research[4] describes the use of a thiolactone derivative of 10-undecenoic acid as a renewable AB′ monomer for the one-pot synthesis of diversely substituted polyamide structures, containing amide moieties both in the polymer backbones and in their side chains. Nucleophilic aminolysis of the thiolactone entity liberates a thiol, which further reacts in a stepwise thiol−ene photopolymerization reaction. Using different primary amines, several structurally diverse polyamides, with physical properties dependent on the length and chemical identity of the side chain, were obtained. Post-polymerization oxidation of the sulfide linkages in the polymer backbone to their corresponding sulfoxides and sulfones altered the material, with the degree of oxidation having an impact on the final mechanical properties. Furthermore, this mild and straightforward polymerization procedure was applied for the synthesis of functional polymer networks.



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L21

MacroRAFT Agents from Renewable Resources and their Use as Polymeric Scaffolds in a Grafting from Approach

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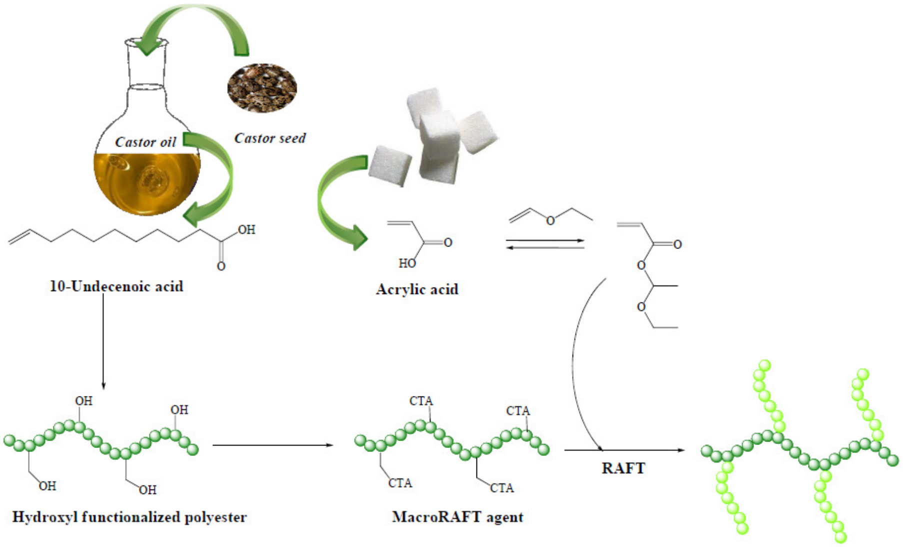
A lot of research has been done to produce bulk chemicals from renewable resources due to the increase in oil price and depletion of the fossil resources. This trend is also found in polymer chemistry. However, also renewable polymer additives gained more interest. These additives often consist of segmented structures to be used as emulsifiers or compatibilizers for example.

In this work we present the synthesis of amphiphilic graft copolymers made from renewable resources via a “grafting from” strategy. First, a linear hydroxyl functionalized aliphatic polyester, prepared from 10-undecenoic acid, was synthesized by a step wise polymerization. Secondly, trithiocarbonate side groups were attached to the prepared polymer, resulting in the formation of a macroRAFT agent.



This macroRAFT agent was used in a subsequent reversible addition-fragmentation chain transfer polymerization (RAFT) of ethoxyethyl acrylate (EEA). The poly(EEA) grafts in the graft copolymer can easily be transformed into poly(acrylic acid) by a simple heating step[1] , resulting in the formation of amphiphilic graft copolymers consisting of segments that are both finding their origin in renewable resouces. The micellisation behavior and the dispersing properties have been analyzed.[2]

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L22

From Fatty Acid Derived Polymers toward Polyethylene – Thermal Behavior of Polyesters, Polycarbonates and Polyacetals

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Long-chain α,ω-functionalized building blocks derived from fatty acids have recently become available. By biotechnological or synthetic procedures like ω-oxidation,[1] isomerizing alkoxycarbonylation[2] and olefin metathesis,[3] monomers for polycondensation reactions are accessible. Polymerization of 1,19- and 1,23-diesters with the corresponding α,ω-diols based on oleic acid and erucic acid, respectively, yields polyester-19,19 and polyester-23,23 with melting points of 103 °C and 108 °C.[4] These polyethylene-like materials can be processed by injection molding or film extrusion. Their melting points are advantageously high compared to existing shorter chain aliphatic polyesters. However, they are still significantly lower than linear polyethylene (Tm = 134 °C). Enlargement of the aliphatic chain between the ester moieties in polyester-30,30,[5] polyester-38,23 and polyester-44,23,[6] generated by multi-step syntheses, only leads to a small increase of Tm. Consequently, the length of the aliphatic chain between the functional groups in polyesters needs to be increased further to converge toward polyethylene. However, synthesis of even longer chain monomers becomes more and more tedious. This problem can be circumvented by applying aliphatic diene metathesis (ADMET) copolymerization of an ester functionalized α,ω-diene and a non-functionalized α,ω-diene, followed by exhaustive hydrogenation of the carbon carbon double bonds.[7] The amounts of ester groups in the resulting polyesters can be regulated via the monomer ratios utilized for polymerization. These random, long-spaced polyesters close the gap between polyesters from classical A2 + B2 polycondensations and linear polyethylene. The same principle can also be applied for other functionalized polymers. Polycarbonates and polyacetals derived from long-chain α,ω-diol polycondensation with dimethylcarbonate and diethoxy methane, respectively, display melting points < 100 °C and can be converged toward polyethylene with the same technique. These findings allow reliable descriptions and predictions of the melting points of very long-spaced ester, carbonate and acetal functionalized polymers.

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L23

Novel Biobased Nonisocyanate Polyurethanes from Dimer Diamines Obtained from Solvent and Catalyst-free Synthesis: Study of the Structure-Properties Relationships

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Polyurethanes (PU) are traditionally synthesized from the reaction between polyols and isocyanates [1,2]. These latter are nevertheless dangerous for the human health. Isocyanates are harmful and potential carcinogenic compounds [3]. A repetitive exposure to them can lead to serious and incurable respiratory problems. Moreover, the synthesis of isocyanates requires the use of noxious substances such as phosgene. They could be partially banned or restricted in the future. Nowadays, a significant attention is paid to environmental and health concerns with a new range of PU called nonisocyanate polyurethanes (NIPU). One of the main ways to obtain NIPU is the aminolysis synthesis. Thus, PU without isocyanate can be prepared via the amine-cyclocarbonate reaction. The substitution of fossil-based products by natural and renewable resources has become a major economic and environmental target, especially in the field of materials [4]. In this light, new promising biobased building blocks such as dimer diamines from vegetable oils can be used for polymer synthesis. Dimer diamines result from the dimerization of two unsaturated fatty acids (from vegetable oils), followed by the replacement of the acid end groups by amine ones. Thanks to their chemical natures and structures, the dimer diamines bring a high flexibility and a low glass transition temperature. Besides, at ambient temperature, this chemical shows a low viscosity, which is a great advantage to develop solvent-free synthesis. In the present study, original biobased NIPU have been synthesized from dimer-based diamines and sebacic biscyclocarbonate in bulk and without catalyst. Biscyclocarbonates and NIPU have been well characterized by FTIR and NMR spectroscopy. A first study has been conducted to determine the optimal carbonate/amine ratio. The influence of different average-amine-functionalities, varying from 2.0 to 2.2, on the structures and properties of NIPU has been investigated by DSC, SEC and dynamic rheological analyses. Based on the FTIR analyses, it has been found that the stoichiometric ratio was optimal for the NIPU synthesis. Although the synthesized polyurethanes show lower molar masses compared to conventional ones, a higher structuration has been observed when the average functionality of the dimer diamine increased. As expected, the glass transition temperatures also raised. Different samples have been synthesized with various behaviors. For instance, thermoset-like materials have been obtained with an average-amine-functionality of 2.15 and 2.2, respectively. Additional analysis (uniaxial tensile tests …) have been performed to analyse the structure-properties relationships of this new class of biobased material. These biobased NIPU appear to be a promising healthy and environmentally friendly alternative to conventional PU. However, still now, the kinetics of the reaction and the final molar masses of the materials are still a great challenge, as for most of the NIPUs synthesis [5].

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L24

Microbial Single Cell Oils - State of the Art and Challenges

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In this lecture a survey will be given on the nature and state of art of the production of microbial single cell oils. Microbial single cell oils are triacylglycerols which are produced intracellularily by so-called "oleaginous microorganisms" as storage lipids. They contain a similar fatty acid composition as plant oils and could therefore be a suitable alternative as starting materials for industrial applications, as they do not compete with food and feed (Ratledge and Cohen, 2005). Certain yeasts, fungi, bacteria and microalgae belong to the group of oleaginous microorganisms. They all share the special feature to have more than 20% lipids in their cellular dry weight. Whenever they are nitrogen limited, the cell division is interrupted, but at a concurrent carbon excess, the carbon will be converted into SCOs as storage lipids. The amount of lipid can reach up to 70 % of the cellular dry weight (Ratledge and Cohen, 2008). Depending on the chosen microorganism, different carbon and energy sources are required. CO_2 and sunlight as zero-cost carbon sources for microalgae represent an advantage for photoautotrophic microalgae. In contrast, producing SCOs with heterotrophic microorganisms like yeasts, fungi and bacteria require carbohydrate rich substances as substrates. Usually glucose and sucrose are the substrate of choice as they are easily accessible from agricultural crops, but also waste substrates like whey from cheese industry or glycerol from biodiesel production can be used. The main components of SCOs are saturated fatty acids including palmitic acid (16:0) and stearic acid (18:0), but they can also contain high amounts of unsaturated fatty acids with carbon chain lengths of sixteen and eighteen (16:1, 18:1, 18:2, 18:3), there under especially polyunsaturated fatty acids (PUFAs) with high value for industrial applications (Meng et al., 2009). SCOs are interesting intermediates for several industrial applications. Due to their chemical functionality available in their structure they are excellent bio resources for the production of detergents, biopolymers and other oleochemicals (Verhé, 2010). Because of their high amounts of polyunsaturated fatty acids, SCOs are also suited for high value products in the cosmetics, food and pharmaceutical Linolenic acid (GLA,–γindustry (Schoerken and Kempers 2009). 18:3(n–6)) for example is a ω-6-fatty acid with anticancerous and anti-inflammatory properties and can therefore be used as dietary supplement for treating problems with inflammation and auto-immune diseases. Even though much research effort was put into the production of SCOs in the last 30 years, only six processes could be commercialized, including the production of cacao butter equivalent (CBE), gamma linolenic acid (GLA), docosahexanoic acid (DHA) and arachidonic acid (AA). However, each commercialization attempt failed because of lower cost alternatives on the market (Ratledge and Cohen 2005). The answers to this problem mainly can be (i) cost reduction via less or zero-cost carbon sources, (ii) optimization of production processes, e.g. with sequential batch technology, (iii) reducing the energy consumption during downstream processing or (iv) the attempt to produce only high value oils (e.g. PUFAs). Besides the costs for the raw material, the downstream processing including extraction, separation and purification of the intracellular SCOs has to be optimized. Further solutions to optimize SCOs production can be (v) screening of new suitable oleaginous microorganisms able to convert low-cost carbon sources into SCOs and (vi) strain optimization by metabolic engineering.

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L25

Microbial Oil as a Renewable Feedstock: Improving Single Cell Oil Properties by Metabolic Engineering

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Fats and Oils are renewable raw materials in the chemical industry with widespread possibilities considered a feasible alternative to the limited and pollutants fossil oils. Recently, microbial oils, also called Single Cell Oils (SCOs), are emerging as beneficial renewable feedstock.

SCOs have several advantages over plant, animal or fossil oil sources as they are not affected by climate and season conditions, they can use a wide range of inexpensive carbon sources, they have short life cycles with rapid growth rates and they can be grown in bioreactor which are easily scaled up in order to accommodate to market needs. Additionally, they can be easily engineered to be enriched in specific oils that can be directly used as lubricants, functional polymers and other high-value fine chemicals, such as pharmaceuticals and nutraceuticals.

Ashbya gossypii is an industrial friendly filamentous fungus and we have recently engineered it to become an oleaginous fungus able to accumulate up to 70% of its cell dry weight as oils. We now wanted to use this modified strain for further metabolic engineering in order to produce interesting building blocks for the chemical industry and here we will discuss our results.

During the last years several microorganism has been engineered to produce fatty acid-derived compounds of industrial interest. We modified the fatty acid elongation and desaturation system of Ashbya gossypii in order to tune the carbon chain length and the number of double bonds of the accumulated oils. Besides, fatty acids have been in vivo derivatized by metabolic engineering and synthetic biology to produce dicarboxylic acids, ricinoleic acid, limonene, alkenes, terpenes and so on. Interestingly ricinoleic acid from castor oil presents serious limitations in its large scale production and toxicity which can be overcame by its production by microbial metabolic engineering.

Therefore metabolic engineering of SCO can directly produce oil derived precursors for chemical industry since we can enrich microbial oils in the desired compound for each application on an inexpensive and renewable way.

L26

Synthesis of Aliphatic α-Branched Aldehydes *via* Combination of a Chemocatalytic Aldol Condensation and an Enzymatic C=C Reduction

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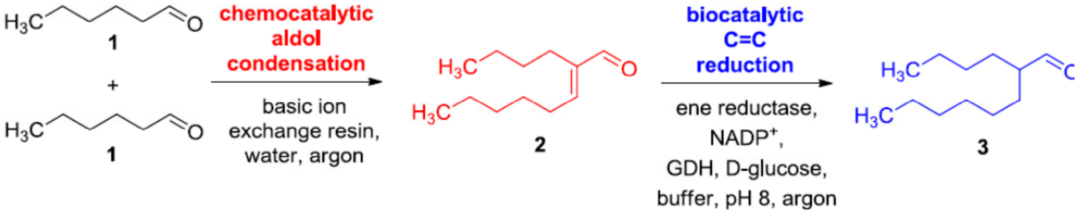
Catalytic processes for the synthesis of aliphatic alpha-branched aldehydes are of wide interest since these molecules are valuable intermediates in the production of a range of industrial chemicals. Representative examples are the specialty chemical 2-ethylhexanol as well as the so-called Guerbet-alcohols as higher homologues thereof with applications in the fields of, e.g., lubricants, plasticizers and surfactants. Whereas today´s technical routes to aliphatic alpha-branched aldehydes are based on pure chemical reaction sequences, integration of enzymatic key steps in modified chemical multi-step processes represents a further exciting opportunity, which could benefit from the advantages of biocatalysis such as, e.g., high selectivity and smooth reaction conditions. The synthesis of aliphatic alpha-branched aldehydes by applying this concept of a chemoenzymatic process (ideally in a one-pot fashion) could be conducted by means of an initial chemocatalytic aldol condensation starting from an aliphatic aldehyde and a subsequent enzymatic C=C reduction of the aldol condensation product. Thus, in continuation of our studies on chemoenzymatic one-pot processes we became interested in the search for a suitable biocatalyst for the reduction of 2-butyl-2-octenal (**2**) as a model compound for aliphatic alpha-branched aldehydes as well as the combination of this biotransformation with a chemocatalytic synthesis of **2** towards a two-step one-pot process (Scheme 1).



Scheme 1. Chemoenzymatic synthesis of aliphatic α-branched aldehydes.

The initial aldol condensation starting from hexanal (**1**) runs efficiently in water in the presence of a strongly basic ion exchange resin as a catalyst. For the subsequent biotransformation a NADPH-dependent ene reductase from Gluconobacter oxydans turned out to be a suitable biocatalyst in combination with a glucose dehydrogenase and D-glucose for in situ-cofactor regeneration. Preliminary application of an immobilized biocatalyst was also successful and revealed the opportunity for catalyst recycling. For both reaction steps, namely aldol condensation as well as enzymatic reduction, suppression of a rapid spontaneous oxidation of the aldehyde moiety in aqueous reaction media turned out to be a critical issue. Thus, both reactions were conducted under argon atmosphere. In this contribution, the development and optimization of the individual reaction steps as well as options for their combination towards a one-pot process will be presented and discussed.

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L27

Large-ring Lactones from Fatty Acids

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The isomerizing alkoxycarbonylation[1] has been proven to be a powerful way for the synthesis of valuables from plant oils. Unsaturated fatty acid esters, with their long-chain hydrocarbon segments can be converted into long-chain aliphatic *α,ω*-diesters and into other compounds successively. As a result of the crystallizable segments generated by full molecular incorporation of the fatty acid feedstock, polyesters with exceptionally high melting and crystallization points are accessible.[2] Due to the step-growth character of the underlying polymerizations, molecular weights are limited. For this reason, chain-growth polymerizations appeared interesting to study.

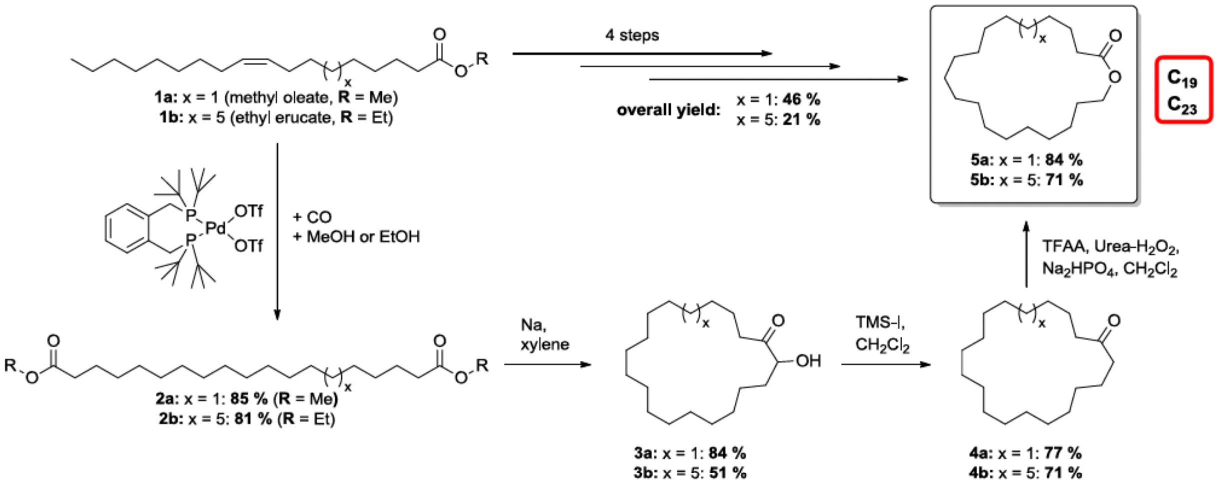

Figure 1. Synthesis route of macrocyclic lactones from fatty acid esters.[3]

Starting from monounsaturated fatty acid esters a four-step synthesis approach yields the macrocyclic lactones in polymerization grade purity (> 99 %). Key step in this synthesis is an acyloin condensation of *α,ω*-diesters **2a** and **2b** to cyclic acyloins **3a** and **3b**, respectively. With the macrocyclic lactones accessible in high purity on a preparative scale ring-opening polymerizations (ROPs) were accessible. Since thermodynamical data for the ring-opening of various large ring lactones[4] do not reveal any trends for the fundamental reactivity of macrocyclic compounds it was interesting to find that ROP of nonadecalactone (**5a**) with aluminum salen complexes leads to polyesters with a molecular weight of $M_n = 10^4$ g/mol. Higher molecular weights can be obtained *via* enzymatic ROP using Novozym N435.

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L28

Esters of Oligo-(Glycerol Carbonate-Glycerol Ether) as Alternative to Fossil Surfactants

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Glycerol carbonate is one of the most attractive glycerol-derived compound due to its multifunctional interesting properties : low melting point(-66.7℃), high boiling point (351℃) besides high dipolar moment (μ = 5.4 D) and dielectric constant values (ε = 109.7). Glycerol is an important by-product derived from the oleochemical industry with high polar and solvent properties (ε = 78.50, μ = 1.67 D, relative polarity = 0.812). Oligomerization of the glycerol carbonate assisted by the glycerol results in the production of polyhydroxylated oligomers rich in linear carbonate functions . To obtain the polyesters of oligocarbonates, we realized the catalytic acylation reaction of these polyhydroxylated oligocarbonates by acyl donor such as methyl esters, fatty acids and vegetal oils . Polar moieties come from glycerol and glycerol carbonate instead of ethylene oxide in most of commercial surfactants, and such oligomers with relative low molecular weight (<1000 d) present better performances. We showed that the insertion of linear carbonate function in the glycerylic skeleton confers to the oligomers an amphiphilic character decreasing the air/water surface tension at 57 mN/m. Controlling the acylation reaction, total acylation or partial acylation, and the nature of acyl donor, high oleic sunflower fatty acids or coprah fatty acids, the physico-chemical properties were improved and oriented. Oligoesters of coprah present the best surface-active properties (cmc, cac < 1 mg/mL, πcmc/cac < 30 mN/m), better than fossil molecule like ethylene glycol monododecyl ether with different ethylene oxide (EO) contents (EO = 4 - 8) , or other ethoxylated surfactants like other ethers of glycol, esters of glycol, ethoxylated monoglycerides, ethoxylated diglycerides, ethoxylated triglycerides and fatty acid esters of sorbitan polyethoxylates . The oligo-(glycerol carbonate-glycerol ether) esters are then usable at reduce concentrations. The self-assembling properties highlighted by polarized optical microscopy in polar solvent were demonstrated. Lamellar phases were observed for oligocarbonates. This organization favours their lubricant properties. Esters of oligocarbonate are few miscible in polar solvents but self-organize when brought into it. Thus they can act as emulsion stabilizer. The oligo-(glycerol carbonate-glycerol ether) esters are amphiphilic molecules with relative low molecular weight with properties of relative high molecular weight molecules. The chemistry of oligomerization of glycerol carbonate presents a “green” alternative to ethoxylated molecules.

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L29

Biodiesel Synthesis Using Centrifugal Contactor-separators: an Example of Process Intensification

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Biodiesel is a very attractive biofuel that is produced from various virgin plant oils as well as waste cooking oils. In 2009, the EU passed the Renewable Energy Directive (RED) which effectively established that renewable energy should account for 10 per cent of the energy consumed in the transportation sector by 2020. This has stimulated the production biodiesel in Europe substantially.

Conventional biodiesel production involves trans-esterification of a plant oil with methanol in combination with a suitable catalyst in either a batch or continuous reactor. New reactor and process configurations are currently actively being pursued. We here report the use of Continuous Centrifugal Contactor Separators (CCCS) for the synthesis of biodiesel using a range of oils and alcohols. In the device, the biodiesel reaction and biodiesel-glycerol separation are combined in a single device. The CCCS (Fig. 1) basically consists of a hollow rotating centrifuge in a static reactor house. The oil and alcohol enter the device in the annular zone between the static housing and the rotating centrifuge, where they are intensely mixed. The formed dispersion is then transferred into the hollow centrifuge, through a hole in the bottom. Here the product phases (biodiesel and glycerol) are separated by centrifugal forces up to 900 g, allowing excellent separation of the fluids.

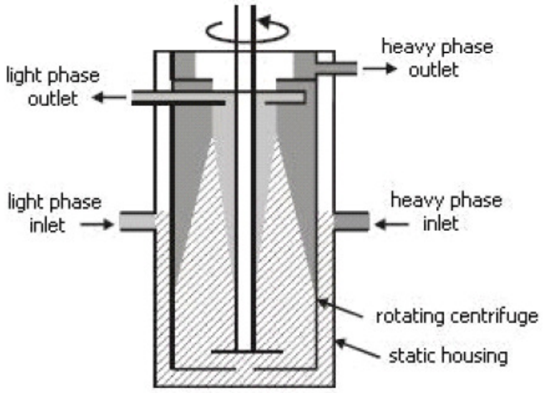

Fig. 1. Cross-sectional view of the CCCS. Hatched: dispersion, light grey: light phase, darker grey: heavy phase

The CCCS devices not only can be used for the initial reaction and product separation but also for the subsequent biodiesel washing step. In this presentation, the performance of the CCCS devices for biodiesel production and the potential use of the devices in mobile biodiesel units will be discussed.

L30

Oxidation Stability of *Jatropha curcas* Biodiesel Produced from High Free Fatty Acid Oil

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Jatropha curcas biodiesel is one of the attractive alternatives for substituting petro diesel. However, due to its natural characteristics of Jatropha curcas oil, this fuel tends to be easily oxidized and decomposed. Decomposition of biodiesel will affect fuel behavior and quality, namely due to changes in acid value, iodine value and viscosity. In the application of biodiesel on the Internal Combustion engine, the changes on such quality parameters might cause its failure due to fuel filter plugging, deposits in the injection system and in the combustion chamber as well as corrosion of metal parts of the engine.
Lower limit for biodiesel oxidation stability under EN 14214 is 6 hours Induction Period (IP) on Rancimat and most of the biodiesel produced from vegetable oils, being rich in unsaturated fatty acids, does not meet this regulation. For this reason, application of antioxidants is generally required to increase the IP to meet the standard.
In the present work, Jatropha curcas biodiesel was produced from high Free Fatty Acid raw Jatropha curcas oil (initial acid value 35.37 mg KOH g-1) without any pre-treatment. The production route consisted of a two-step method, using acid esterification (catalyzed by H2SO4) followed by basic transesterification (catalyzed by KOH) with methanol. The oxidation stability of biodiesel was measured using Rancimat (EN 14112) and the effect of Pyrogallol antioxidant on IP was evaluated at different concentrations (up to 1000 mg L-1). It was found that Jatropha curcas biodiesel without antioxidant did not fulfill the standard requirement, since the Rancimat IP of the product was 1.37 h. By evaluating the different concentrations of Pyrogallol antioxidant it was found that, in order to meet the 6 h IP, it might be used effectively, at a concentration of at least 120 mg L-1.

L31

Alkenolysis as a Path to Alternative Diesel Fuels Based on Methyl Oleate

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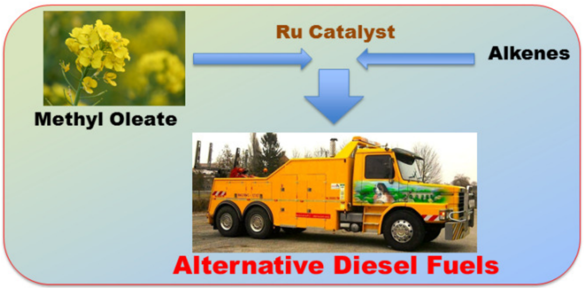
Hydrocarbons are the backbone of almost all present transportation systems in a world with increasing mobility. As petroleum feedstock dwindles, the need to find alternative fuels is gradually increasing. Fats and oils are the most important available renewable feedstock processed by the chemical industry,[1] leading among other products to biodiesel. However, properties of biodiesel differ from petrodiesel originating from fossil sources. For instance, the stability towards oxidation, higher viscosity and pour point are the main drawbacks of biodiesel towards petrodiesel.[2]

Therefore, proceeding a transformation of biodiesel leading to an alternative fuel with properties closer to those of petrodiesel is necessary.[3] As ethylene can originate from ethanol dehydration[4] and some alkenes from ethylene oligomerisation, some of the obtained diesel fuels are originating from a completely renewable feedstock. The metathesis reactions of commercial grade methyl oleate with six different short chain alkenes (ethylene, 1-butene, 1- and 2-pentene, 4,4-dimethylpent-1-ene and 1-hexene) are performed using four different ruthenium-based catalysts, with catalyst loading as low as 200 ppm in some cases, followed by a tandem hydrogenation of the resulting products. The overall process leads to mixtures of esters and alkanes with most of the properties meeting the DIN specifications for conventional diesel fuels. Two of these mixtures, originating from butenolysis and hexenolysis, were used in a car motor for testing their potential in replacing conventional diesel and presented very interesting properties compared to conventional diesel (lower soot and CO emissions, lower hydrocarbons emissions, slightly lower heating values).



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L32

Ethylene Production from Fats and Oils

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Utilization of fats and oils by deoxygenation to afford renewable fuel components has been studied extensively and even implemented industrially. Apart from fuel production, the product of triglycerides deoxygenation is highly suitable for production of olefins, namely ethylene and propylene, by steam cracking as the yields of these olefins, particularly ethylene, exceed significantly the olefin yields obtained by steam cracking of the conventional feedstock, i.e. naphtha. The contribution will discuss in detail the possibilities of ethylene production from fully as well as partially deoxygenated triglycerides.

Abstracts

Part 2: Posters

P1

Acetalisation of glycerol to value added chemicals

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Biodiesel production is accompanied by the formation of glycerol as a by-product. Glycerol is expected to become a major platform chemical due to the increased biodiesel production. The use of glycerol is limited now, being mainly confined to pharmaceuticals and cosmetics. Hence new processes are needed that can convert the surplus glycerol to value-added chemicals. In addition to taking advantage of the relatively low price of glycerol, this will also improve the economic viability of biodiesel manufacture. Research efforts are gaining momentum for the synthesis of value added products from glycerol. We report solvent-free liquid-phase glycerol acetalisation with acetone using niobia catalysts. Niobia (Nb_2O_5) has been used as a water-tolerant solid acid catalyst for various water-involving reactions. The effect of calcination/pretreatment temperature of hydrated niobium oxide, acidity and other reaction parameters on the catalytic performance was investigated. The results of this study show that niobia acts as a stable active catalyst for glycerol acetalisation, forming 2,2-dimethyl 4-hydroxymethyl- 1,3-dioxolane (solketal) predominantly. The reactions were carried out in the liquid phase in a 50 ml glass reactor equipped with a condenser and a magnetic stirrer. Required amounts of glycerol and acetone were stirred with a specific mass of the catalyst in powder form. To monitor the reaction, samples of the reaction mixture were taken periodically and analysed by gas chromatography. The N2 adsorption–desorption isotherms were measured at 77 K on a Micromeritics ASAP- 2000 after evacuation at 473 K for 5 h. Surface areas were calculated by the BET method. Powder X-ray diffraction pat-terns were collected on a Bruker powder X-ray Diffractometer. The system used for ammonia adsorption flow calorimetry is based on a Setaram 111 DSC with an automated gas flow and switching system. Diffuse reflectance infrared Fourier transform (DRIFT) spectra of adsorbed pyridine were obtained on a Nicolet NEXUS FTIR spectrometer. Acetalisation reactions were conducted at 343 K, with a glycerol: acetone molar ratio of 1 : 1.5 using 6.4 wt% of catalyst without any solvent. The activities were influenced significantly by the calcination temperature. The samples pre-treated at lower tempera-tures were most active while the sample calcined at 973 K was least active. For the samples pre-treated at 473 and 573 K, more than 70% glycerol was converted after 2 h. For the samples calcined at higher temperatures, initial conversions were lower but increased over extended reaction time. Activity of the catalysts is in accordance with their acidity, indicating that higher acidity is favourable for higher catalytic activity.

P2

Photopolymerizable Synthons from Fatty acids and Glycerol Derivatives

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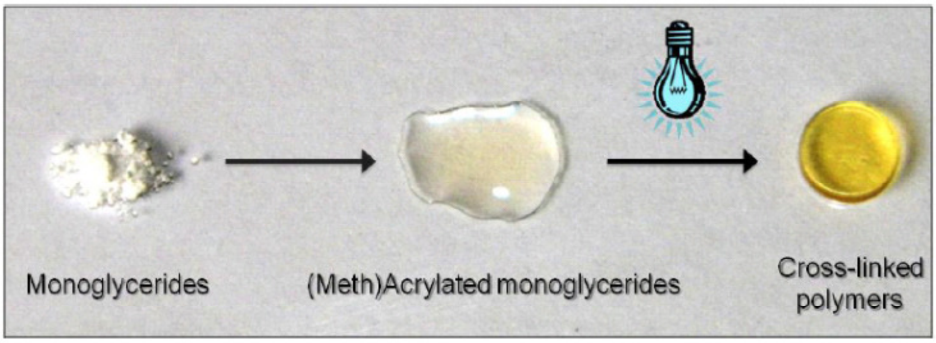
The use of renewable resources for the synthesis of bio-based polymers is a current and growing challenge **[1]**. In this context and in the course of our ongoing studies in Glycerol Chemistry **[2]** and Green Polymerization **[3]**, we report the synthesis of photopolymerizable bio-based monomers according to a two-steps procedure. The first one consists in the synthesis of monoglycerides of high purity, obtained by condensation of fatty acids with either glycerol carbonate or glycidol, in a solvent-free medium and in the presence of tetrabutylammonium iodide (TBAI) as organocatalyst. The obtained bio-based monoglycerides were modified in the second step by reaction with acryloyl and methacryloyl chloride leading to a series of new diacrylated and dimethacrylated monomers. Photopolymerization investigations monitored by infrared spectroscopy were achieved under ultraviolet radiation in the presence of a photoinitiator. The role played by the concentration of photoinitiator, the intensity of irradiation, and the nature of monomers were investigated. Thermal gravimetric analysis, gel content determination, tests of swelling and analysis of the pendulum hardness were also performed on the resulting bio-based photopolymers **[4]**.



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P3

Highly efficient grafting-onto Castor Oil derived Polymers using a Convertible Isocyanide

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The Ugi four component reaction (Ugi-4CR) and the Passerini three component reaction (Passerini-3CR), the most famous isocyanide based multicomponent reactions (IMCRs), were performed with 10-undecenoic acid and 10-undecenal as castor oil based platform chemicals as well as with the convertible isocyanide 2-(2,2-dimethoxyethyl)phenyl isocyanide, to obtain versatile fatty acid derived α,ω-diene monomers.[1],[2],[3] These monomers were polymerized via acyclic diene metathesis polymerization (ADMET),[4] followed by hydrogenation of the double bonds and conversions of the isocyanide moieties to highly reactive indolyl amides under weak acidic conditions. Subsequently, several post-modification reactions of these indolyl amide containing ADMET polymers with different nucleophiles were performed.[5],[6] Under elimination of indole, side-chain modifications to carboxylic acids, esters, secondary and tertiary amides, as well as thioesters led to highly diverse polymers exhibiting different properties.

Thus, we demonstrated that the use of a convertible isocyanide for the synthesis of fatty acid derived polymers applying IMCRs is an excellent grafting-onto method to achieve well-designed polymers.

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P4

Atom-efficient approaches towards diverse substituted polyamides applying the Ugi four-component reaction

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Polyamides and polypeptoids provide many applications due to their material properties, biocompatibility, and possible backbone degradability.[1] Conventional synthetic routes involve the polycondensation of carboxylic acids or esters and amines as AA- or AB-type monomers. Furthermore, the ring-opening polymerization of lactams is industrially applied.[2]

The Ugi-four component-reaction (Ugi-4CR) offers a novel route to a new class of substituted polyamides and polypeptoids.[3,4] The use of two bifunctional components, such as fatty acid derived dicarboxylic acids and diamines, in combination with the two other remaining components of the Ugi-4CR, leads to polymers with defined and "free to choose" side chains. Here, we will discuss several combinations of renewable AA- and BB- type monomers for the synthesis of such diverse polymers using the Ugi-4CR reaction.

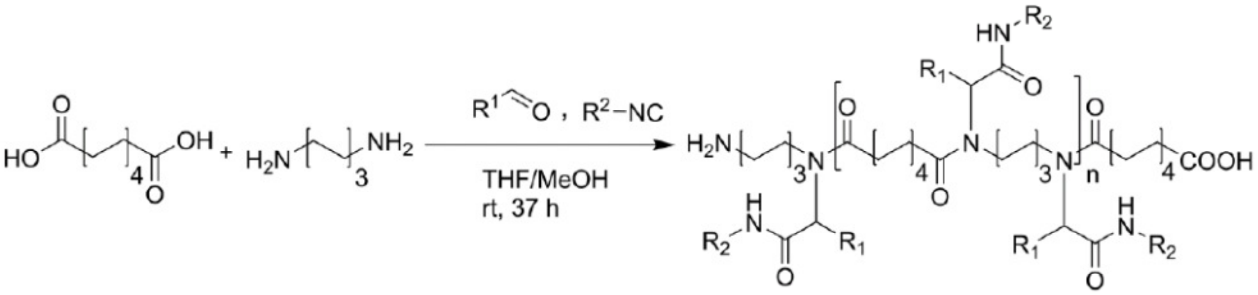

Figure: One of the possible combinations for the polyamide synthesis *via* the Ugi-4CR employing a renewable dicarboxylic acid.

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P5

Renewable polyamides and polyureas derived from plant oils

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Polyamides and polyureas were synthesized from castor oil derived 10-undecenoic acid and sebacic acid (C10-dicarboxylic acid), as well as from azelaic acid (C9-dicarboxylic acid), which can be obtained by oxidative cleavage from Delta-9-unsaturated fatty acids. The olefin self-metathesis of methyl 10-undecenoate generates a C20-diester,[1] which was shown to be a highly valuable monomer for renewable polyesters, -amides and -urethanes in previous works.[2,3] The conversion of C9, C10 and C20-fatty acid dimethyl or diethyl esters to dihydroxamic acids,[4] followed by a novel base-catalyzed, eco-friendly and sustainable Lossen rearrangement,[5] led to the formation of dimethyl carbamates monomers. These monomers were successfully used for an isocyanate-free synthesis of renewable polyureas by base-catalyzed reactions with diamines under neat conditions at high temperatures. Moreover, the saponification of the dimethyl carbamates under harsh basic conditions, gave plant oil derived C7-, C8- and C18-diamines as valuable monomers for the synthesis of renewable polyamides. The combination of the before mentioned diamines with C9-, C10 and C18-fatty acid esters resulted several fully renewable polyamides. The novel polyamides as well as the polyureas were carefully characterized via ^{1}H NMR, GPC, DSC and IR.

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P6

Divergent Dendrimer Synthesis via the Passerini three Component Reaction and Olefin Cross-Metathesis

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The combination of the Passerini reaction [1],[2] and olefin cross-metathesis is shown to be a very useful approach for the divergent synthesis of dendrimers.[3] Castor oil-derived platform chemicals, such as 10-undecenoic acid and 10-undecenal,[4] were reacted in a Passerini reaction with an unsaturated isocyanide to obtain a core unit having three terminal double bonds. Subsequent olefin cross-metathesis with tert butyl acrylate,[5] followed by hydrogenation of the double bonds and hydrolysis of the tert-butyl ester, led to an active core unit bearing three carboxylic acid groups as reactive sites. In iterative steps of the Passerini reaction with 10-undecenal and 10-isocyanodec-1-ene for branching, and olefin cross-metathesis with tert-butyl acrylate followed by hydrogenation and hydrolysis allowed the synthesis of a third generation dendrimer. All steps of the synthesis were carefully characterized by NMR, GPC, MS and IR.

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P7

A two-step synthesis of dicarboxylic acids from homoallylic fatty derivatives using a ruthenium catalyst and H_2 acceptors

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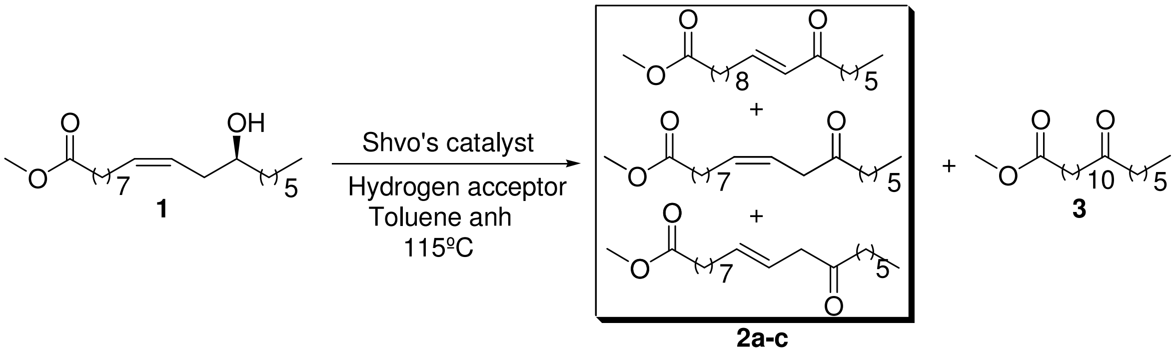
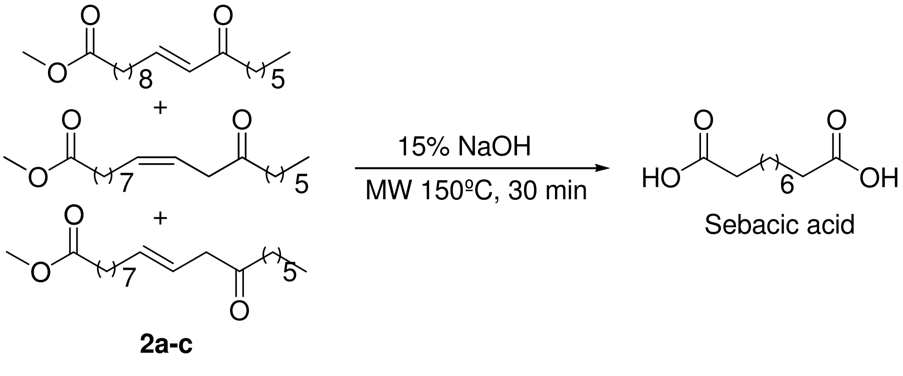
A two-steps alternative synthetic route to prepare dicarboxylic acids from renewable sources is described. The first step consists on the oxidation of homoallylic hydroxyl fatty esters such as methyl ricinoleate (**1**) to the unsaturated oxo compounds (enone, cis and trans isomer **2a**-**c**) using the Shvo's catalyst and a hydrogen acceptor. Low reaction yields were obtained using **1** and common hydrogen acceptors such as acetone or butanone because of the reduction of the enone intermediate **2a** into the corresponding oxo saturated compound (**3**). Hence, a time-depending quantitative screening of 8 aliphatic and 8 aromatic hydrogen acceptors was performed to evaluate their capacity to avoid the reduction of the enone in the oxidation process of methyl ricinoleate. These 16 hydrogen acceptors were chosen on the basis of their relative reduction potentials.



Among them, acrolein and methyl vinyl ketone showed the best results minimizing the formation of the saturated oxo compound. Acrolein was chosen to study the reaction scope for 1 h reaction time. Castor oil, lesquerella oil and derivatives of both were successfully oxidized under the above described conditions. Finally, the unsaturated oxo compounds were used to prepare sebacic and dodecanedioic acids with satisfactory yields. This second step was carried out in a microwave reactor using a 15% NaOH solution for 0.5 h.



P8

Triazolinediones as a versatile click chemistry platform providing functionalization and cross-linking of plant oils

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Recently, more and more research groups started to concentrate on carbohydrate-(starch, cellulose, lactide, chitin & chitosan), plant oil- (vegetable oils, fatty acids) and terpene-(rosin, citrous products) based polymers and synthesis technologies and some of them have even been commercialized to some extent. When the chemical structures of these products are evaluated, one easily realizes that they provide different amounts of double bonds that are available for chemical functionalization. The possibility to use the plant oil directly, without chemical modification or further functionalization, most often leads to cross-linked structures (thermosets, coatings, resins…). A wide range of polymerization and/or functionalization methods, including condensation, radical, cationic and metathesis procedures as well as thiol-ene & yne and azide-alkyne addition reactions have been applied. The scope, limitations, and possibility of utilizing such methods reveal that new robust, non-toxic, energy- & atom-efficient, orthogonal and industrially attractive chemical pathways are still needed.

Here a new click chemistry platform, recently developed by our group[1], based on triazoline diones (TAD) is used to functionalize and cross link plant oils directly in an atom efficient and additive-free manner. Although TAD is known as an identification tool for GC-MS[2] and as functionalization tool for triglycerides[3], we show here for the first time the synthesis of cross-linked polymeric materials based on the reaction of a bifunctional TAD molecule with pure plant oils. In a first stage, model reactions were conducted on fatty acids with a monofunctional TAD component, followed by conducting the same experiment on a range of commercially available plant oils. In a last stage, these plant oils were cross-linked leading to the development of a novel plant oil based network platform

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P9

Easy synthesis of polyolesters with solid acid catalysts

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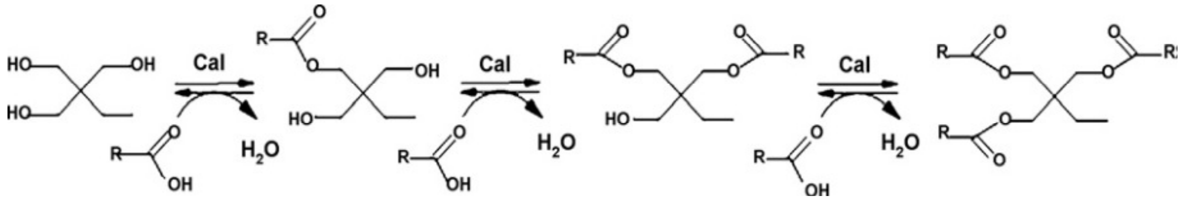
World lubricants consumption is estimated to be around 40 million metric tonnes per year. Automotive and hydraulics are the largest group of sold and used lubricant in the world. About 50% of all sold lubricants are lost in environment, resulting in severe contamination of soil, groundwater and air [1]. As a result, there is an increasing demand for biolubricants derived from vegetable oils. This class of materials is renewable, biodegradable and can be used as an energy source at the end of lifeclycle, to limit the environmental impact [2].
Synthesis of biolubricants is based on the esterification reaction between fatty acids, derived from vegetable oils and polyols, like pentaerythrol (PE) or trimethylolpropane (TMP). The reaction is usually carried out with an homogeneous acidic catalyst . In order to make the reaction more enviromentally friendly we here suggest the use of heterogeneous ones. The heterogeneous catalysts would provide simpler and cheaper separation processes, reduce or eliminate wastes production and in principle could be re-used until deactivation.



Scheme 1: Esterification reaction between TMP and a carboxylic acid

Some experiences in solid acid catalysts, using different modified silicas in order to catalyze the esterification reaction are here presented and discussed. Conversion yields up to 99 % in only 6 hours reaction, with selectivity up to 95% in triesters were obtained [3]. The catalyst can be recycled 6 times at least.
Results obtained in the synthesis of monoglycerides over the same solid catalysts will also be discussed.

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P10

Catalyst Structure-Productivity and Structure-Selectivity Relationship in the Isomerizing Methoxycarbonylation of HO-Sunflower Oil

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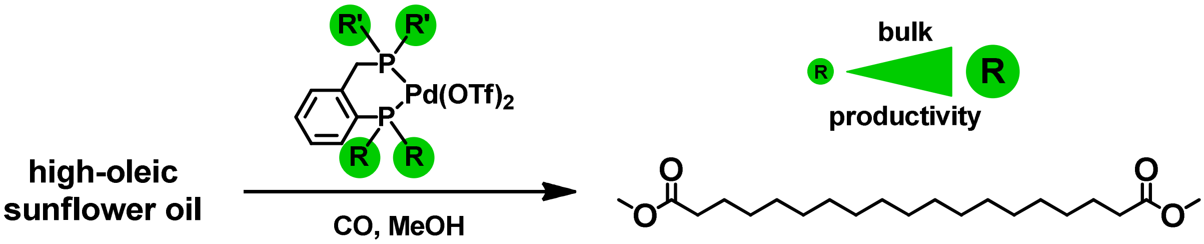
Fatty acids from plant oils are attractive materials for monomer generation, due to their unique long-chain methylene sequences.[1] A full linear incorporation of the entire fatty acid chain into polyesters is desirable not only in order to use the starting material efficiently, but also generates crystallizable sequences which are beneficial for materials properties like modulus. The terminal functionalization of fatty acids is a synthetic challenge, however. Via Palladium(II) catalyzed isomerizing alkoxycarbonylation, fatty acids are transformed into α,ω-functionalized diesters in high selectivity.[2] These diesters are obtained in polycondesation grade purity (> 99.5 %)[2b-c] and are used as platform chemicals for the generation of novel polycondensates such as semi-crystalline aliphatic polyesters,[2b-c] hydrophobic polyamides[2c] or hydrolytically degradable polyacetals.[3]

We have revealed the essential mechanistic features responsible for this unusual selectivity.[2d] However, the question remains how the catalysts' diphosphine substitution pattern impacts selectivity and productivity. This is obviously decisive for enhanced catalyst performance. In this contribution we present the synthesis and evaluation, including mechanistic insights, of a series of Palladium(II) complexes bearing unsymmetrical diphosphines 1,2-$(CH_2PR'_2)(PR_2)C_6H_4$ with variable steric demand, transforming high-oleic sunflower oil into linear diesters with high selectivity (Scheme 1).



Scheme 1: Transformation of HO-sunflower oil into linear diesters with unsymmetrical diphosphine Pd(II) complexes [{1,2-$(CH_2PR_2)(PR'_2)C_6H_4$}$Pd(OTf)_2$].

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P11

Plant-oil based linear long-chain aliphatic polyesters for injection moulding, film extrusion and electrospinning

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Thermoplastic polymers are currently prepared almost exclusively from fossil feedstocks. In view of their limited availability, alternative renewable resources are desirable in the long term.[1,2] More importantly, the unique molecular structure of different renewable feedstocks can provide otherwise inaccessible products and properties. Due to their particular long methylene sequences, fatty acid esters are attractive substrates for monomer generation. In order to fully utilize this potential, a complete linear incorporation of the entire hydrocarbon chain is desirable. This can be brought about by isomerizing alkoxycarbonylation.[3] In this way unsaturated fatty acids are selectively converted into linear α,ω-diesters in polycondensation grade purity.[4,5]

We demonstrate that polycondensation of such long-chain linear diesters and diols can yield polyesters with sufficient molecular weights as reflected by their mechanical properties. Remarkably these polyesters can be processed to films. Blends and electrospinning into non-wovens are also addressed.

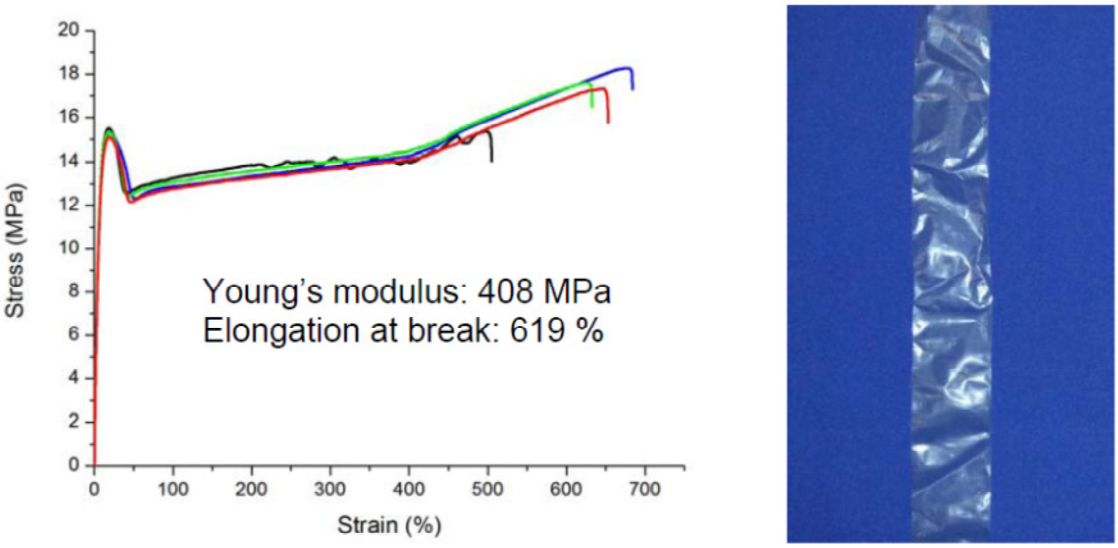

Figure 1: Left: Stress-strain curves (constant drawing rate of 50 mm min^{-1}, room temperature) of PE-19.19. Right: Image of melt-extruded film of PE-19.19.

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P12

Synthesis of renewable segmented polymer structures

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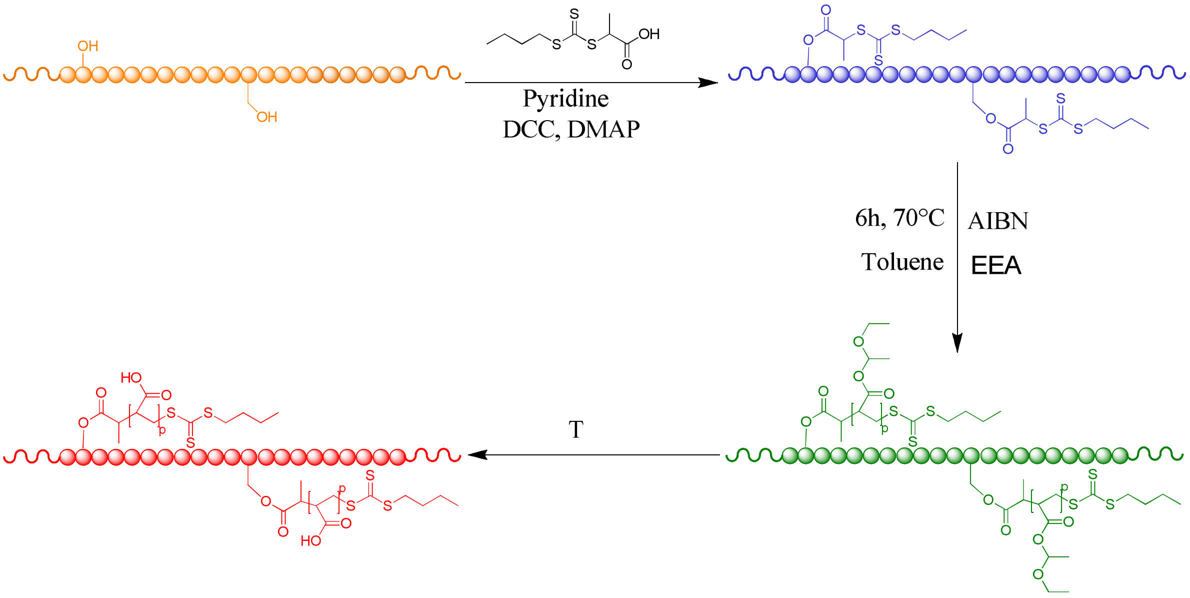
Due to increasing oil prices and the inherent finiteness of fossil fuels, renewable resources gain more importance in the chemical industry. The polymer industry already tried to make bulk polymers from renewable resources but often the lack of some physical and mechanical properties prevented their commercial use. This problem can be overcome by the use of additives such as colorants, stabilizers, surfactants, emulsifiers, preservatives, compatibilizers, and dispersants. This was the starting point to prepare 'green' emulsifiers.

In this work, the synthesis of amphiphilic graft copolymers made from renewable resources via a "grafting from" strategy is presented. In a first step, a linear hydroxyl functionalized aliphatic polyester, prepared from 10-undecenoic acid, was synthesized by a step wise polymerization. Secondly, trithiocarbonate side groups were attached to the prepared polymer, resulting in the formation of a macroRAFT agent. This macroRAFT agent was used in a succeeding reversible addition-fragmentation chain transfer polymerization (RAFT) of ethoxyethyl acrylate (EEA). The poly(EEA) grafts in the graft copolymer can simply be transformed into poly(acrylic acid) by an easy heating step[1] , resulting in the formation of amphiphilic graft copolymers consisting of segments that are both finding their origin in renewable resources. For these polymers, micellisation behavior and the dispersing properties have been analyzed.[2]



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P13

Lipase catalyzed synthesis of emollient esters in deep eutectic solvents

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Lipases are versatile biocatalysts applied industrially e.g. for the synthesis of chiral intermediates, the manufacturing of margarine and omega-3 concentrates for food application and the production of emollient esters for the cosmetic industry [1,2]. Technical emollient ester synthesis is done with immobilized lipase B from Candida antarctica under a high vacuum for water removal, which drives the esterification reaction towards completion. It was shown in a life cycle assessment that the enzymatic route is superior to the chemical manufacturing regarding environmental aspects [3,4]. Here we present a new biocatalytic approach to synthesize emollient esters in good yield without water removal. We were able to utilize non-immobilized lipase dissolved in deep eutectic solvents (DES) in a two phase system consisting of the lipidic substrate phase and the hydrophilic solvent phase. DES are non-volatile solvents consisting of a quaternary ammonium salt and a hydrogen bond donor, as e.g. a mixture of choline chloride and urea with an eutectic melting point of 12℃ [5]. It was shown already that several enzymes including lipases exhibit activity in DES though they consist of strongly denaturing urea [6,7]. In our study the biocatalytic reaction in DES was compared to other solvent systems and the differences in reaction velocity and equilibrium conditions for immobilized and non-immobilized lipase B from Candida antarctica were analyzed. Optimized reaction conditions were elucidated for the synthesis of decyl oleate and decyl laurate by varying e.g. substrate to solvent ratio, water content, lipase concentration and temperature. Additionally a variety of other emollients were synthesized in lab scale under optimized reaction conditions. Purification of the product can be done by simply separating the DES phase and washing or refining the final emollient ester, thus making the synthesis industrially feasible.

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P14

Terpene based polyesters via isomerizing methoxycarbonylation

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Polymeric materials from renewable resources are attractive from different perspectives. The limited availability of fossil feedstocks like oil and gas may require alternative sources on the very long term,[1] and renewable feedstocks can possess unique molecular structures. Providing they can be translated into the (polymer) product by appropriate synthetic routes, they may exhibit useful properties.
To this end, terpenes are an interesting class of substrates due to their rich variety of functional groups like hydroxy, carboxy and olefins in different terpenes. A characteristic of many terpenes however, is their susceptibility for rearrangements and other undesired side reactions. A stimulus for this work were recent findings of very selective conversions of internal double bonds to linear primary esters *via* isomerizing alkoxycarbonylation.[2,3] As part of our ongoing studies of terpenes as a renewable resource[4] we have synthesized monomers for polycondensation reactions *via* isomerizing alkoxycarbonylation. Citronellic acid, citronellol, and dihydromyrcenol (Figure 1) were converted selectively into primary diesters or hydroxy esters, respectively, which were then used in polyester synthesis. This is also the case for eugenol as a related substrate which is attractive as it can be generated from lignin waste potentially.[5]

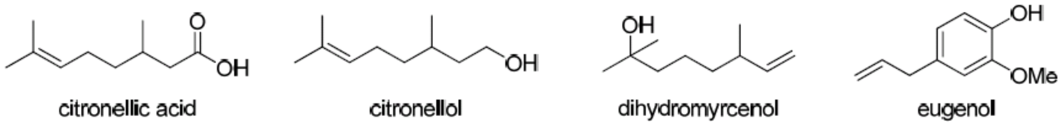

Figure 1: Starting materials for isomerizing alkoxycarbonylation reaction.

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P15

Oils and Free fatty acids for the synthesis of biosurfactant mannosylerythritol lipids by Pseudozyma Species

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Biosurfactants (BS) are microbial surface-active compounds that have unique physical and chemical properties, such as low toxicity, biodegradability, foaming, and functionality under extreme conditions, among others. One of the most promising class of biosurfactants currently known are the Mannosylerythritol lipids (MEL), glycolipids produced in high concentration by Pseudozyma species in the presence of fatty acids. MEL may be composed of a group of four variants (A to D), which are classified by the degree in acetylation, which affects the polarity of the biosurfactant and by that their spectrum of application. Individual strains produce individual MEL mixtures which also depend on the raw material used (fatty acid chain length, unsaturation, etc). Therefore we evaluated the effect of different raw materials such as olive oil (C18:1), soybean oil (C18:2), coconut oil (C12) and ricinoleic acid free fatty acids (C18:1, 12-OH) on the production of MEL in different Pseudozyma strains. In general oils such as, soybean or olive oil containing long chain and unsaturated fatty acids were found to be best inducers of MEL production. However, significant differences between strains were observed. MEL A-strain produced MELs with all raw materials with comparable end concentration. In contrast, MEL B- strain produced low concentrations of biosurfactant with every substrate, indicating low activity of the MEL-pathway in general. MEL C –strains responded to different substrates by varying production rates as well as different product mixtures. Thus depending on the strain and the feed of raw material, product concentration and composition can be modulated. We are currently in the process to analyze the molecular details responsible for these differences. Our results show that MELs can be produced from a variety of renewable oil substrates resulting in different product spectra which can be tailored to the needs of various industrial applications.

P16

Synthesis, characterization and electronic application of poly (linoleic acid)-g poly(methyl methacrylate) graft copolymer

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Poly (linoleic acid)-g-poly(methyl methacrylate) (PLiMMA) graft copolymer was synthesized and characterized. PLiMMA graft copolymer was synthesized from polymeric linoleic acid peroxide (PLina) possessing peroxide groups in the main chain by free radical polymerization of methyl methacrylate. Later, PLiMMA was characterized by proton nuclear magnetic resonance (1H NMR), gel permeation chromatography (GPC), thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) techniques. Furthermore, Au/PLiMMA/n-Si diode was fabricated for the purpose of investigating PLiMMA's conformity in diodes. The main electrical characteristics of this diode were investigated using experimental current-voltage (I-V) measurements in dark and at room temperature. Obtained results, such as sufficiently high rectifying ratio of 4.5x104, indicates that PLiMMA is a promising organic material for electronic device applications.

P17

Illumination effect on electrical characterization of Au/poly (linoleic acid)-g-poly(methyl methacrylate) (PLiMMA)/n-Si diode

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The poly (linoleic acid)-g-poly(methyl methacrylate) (PLiMMA) used firstly as an interfacial layer in a Schottky diode. Main electrical characteristics of the Au/poly (linoleic acid)-g-poly(methyl methacrylate) (PLiMMA)/n-Si diode were investigated. This investigation was realized by using I–V measurements in dark and under illumination at room temperature. It is found that n, and values of the diode are for dark and 100 mW/cm2Ω; 6.3, 0.71 eV, 676 Ω2.8, 0.87 eV, 8096 illumination intensity, respectively. Also, reasons of the deviation from the ideal thermionic emission theory were investigated using Cheung&Cheung method and Card&Rhoderick's function for B(V)), seriesΦcalculating voltage dependence of barrier height (resistance ( ) and number of surface states (Nss) of the Au/PLiMMA/n-Si diode.

P18

Synthesis and Characterization of New Poly(linoleic acid) Graft Copolymers

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Synthesis of graft copolymers by ring-opening polymerization and free radical polymerization using polymeric linoleic acid peroxide (PLina) is reported. Graft copolymers having structures of poly(linoleic acid)-g-poly(lactid)-g-poly(methyl methacrylate) were synthesized from PLina, possessing peroxide groups on the main chain by the combination of free radical polymerization of methyl methacrylate and ring-opening polymerization of D,L-lactid in one-step. Principal parameters, such as monomer concentration, initiator concentration, and polymerization time, which effect the one-pot polymerization reactions were evaluated. The obtained graft copolymers were characterized by 1H NMR spectroscopy, gel permeation chromatography, thermal gravimetric analysis and differential scanning calorimetry techniques.

P19

Hydroxylation of Oil/Oily Acid Peroxides for Synthesis of Graft Copolymers

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Linoleic acid and soya oil was exposed to air under sunlight to obtain autoxidized linoleic acid and soya oil peroxides, respectively. Oxidized linoleic acid and soya oil was allowed to react with diethanol amine to obtain hydroxylated linoleic acid and soya oil polymer. Biodegradable poly (linoleic acid)-g-poly(ε-caprolactone) graft copolymers were synthesized via ring opening polymerization between autoxidized linoleic acid peroxide initiators's carboxylic acid groups and ε-caprolactone monomer.The graft copolymers were characterized using proton nuclear magnetic resonance (1H NMR), Fourier Transform Infrared Spectroscopy (FT-IR), gel permeation chromatography (GPC), thermal gravimetric analysis (TGA), and differential scanning calorimetry (DSC) techniques.

P20

Synthesis and Characterization of New Polyesters Containing Pendent Pentadecyl Chains

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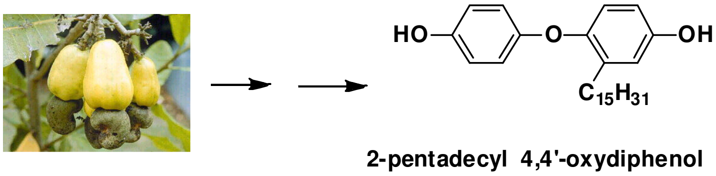
A new bisphenol *viz.*, 2-pentadecyl 4,4'-oxydiphenol was synthesized starting from cashew nut shell liquid (CNSL) – a by-product of the cashew processing industry. [1]



2-pentadecyl 4,4'-oxydiphenol

A series of new aromatic polyesters containing pendant pentadecyl chains was synthesized by interfacial polycondensation of 2-pentadecyl 4,4'-oxydiphenol with terephthalic acid chloride (TPC), isophthalic acid chloride (IPC) and a mixture of TPC and IPC (50:50 mol %). A series of copolyesters was synthesized from varying mixture of 4,4′-isopropylidenediphenol and 2-pentadecyl 4,4'-oxydiphenol with TPC. Inherent viscosities of polyesters and copolyesters were in the range 0.70–1.21 dL g^{-1} and number-average molecular weights were in the range 16,000–48,200. Polyesters containing pendant pentadecyl chains dissolved readily in organic solvents such as chloroform, dichloromethane, pyridine and *m*-cresol and could be cast into transparent, flexible and tough films from chloroform solution. Wide-angle X-ray diffraction data revealed amorphous nature of the polyesters containing pendent pentadecyl chains. The formation of loosely developed layered structure was observed due to the packing of pendant pentadecyl chains. The temperature at 10% weight loss (T_{10}), determined using thermogravimetric analysis in nitrogen atmosphere, of the polyesters containing pendant pentadecyl chains was in the range 430–460°C indicating their good thermal stability. Polyesters and copolyesters exhibited glass transition temperatures (Tg) in the range 29–47°C and 147–202°C, respectively. A large difference between glass transition (29–202°C) and T_{10} (430-460°C) values of aromatic polyesters containing pendent pentadecyl chains offers a wide processing window.[2]

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P21

Synthesis, properties and combustion behaviour of alternative diesel fuels originating from renewable resources

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In this poster we describe a joint research project between the Likat and the Institute of Piston Machines and Internal Combustion Engines at the University of Rostock. The aim was to derive fuels from vegetable oils and its derivatives in a first step and to determine its fuel properties and combustion behaviour in a second step.

On one hand fatty acid methyl esters (methyl oleate, rapeseed oil methyl ester) were used, on the other hand domestic vegetable oils were applied directly. The focus was set on metathesis1 with subsequent hydrogenation in tandem reaction.2 Originating from various starting materials and different reactions and work-up processes3, a variety of fuel-like product mixtures could be generated by the Likat and made available to the Faculty of Mechanical Engineering and Marine Technology, Institute of Piston Machines and Internal Combustion Engines. Regarding their measured fuel properties the feasibility of synthesising diesel-like product mixtures by metathesis of fatty acid derivatives could be demonstrated. Boiling curves and physical parameters show good accordance with conventional diesel.

In respect to hexenolysis a scale-up was possible from 3 mL for first experiments to 3 L for the production of large amounts. Thus, ca. 15 kg of a diesel-like fuel could be generated which was used directly in a subsequent motor test. Other results formed the background for one further motor test based on a mixture of model compounds. Exhaust gas emissions were measured at several operation points revealing a slight reduction of most hazard compounds in comparison to conventional diesel.

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P22

Cyanoethylation of glycerol

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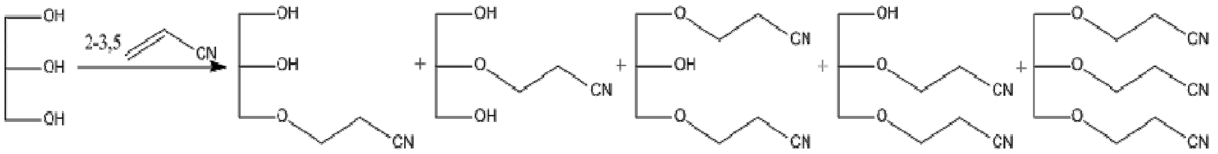
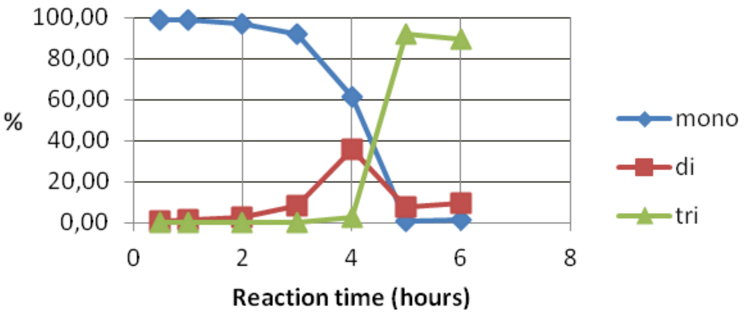
In the last few years, the glycerol production has surpassed 2 million tons in the world from biodiesel industry. So, many new applications of glycerol have appeared and an increasing number of works is led in this area: glycerol becomes a building bloc in organic chemistry [1]. The esterification, transesterification or acylation reaction is generally used to functionalize glycerol to give mono-, di- or tri-glyceride products. However, the ester function is found to be more sensitive to hydrolyse than ether unit.



In this communication, we reinvestigate the nucleophilic addition of glycerol on acrylonitrile which was descrided by Bruson [2]. The cyanoethylation of glycerol was interesting because the cyano group can be easily converted to amine, alkylester, amide for further functionalizations. The reaction was reached without organic solvent and mono-, di- and tri-substituted products are monitored by GC after silylation.

Ratio of mono-, di- and tri-2-(cyanoethyl)glycerol in the reaction mixture



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P23

Novel techniques to optically characterize melt crystallization kinetics of high oleic sunflower oil based fatty acid mixture

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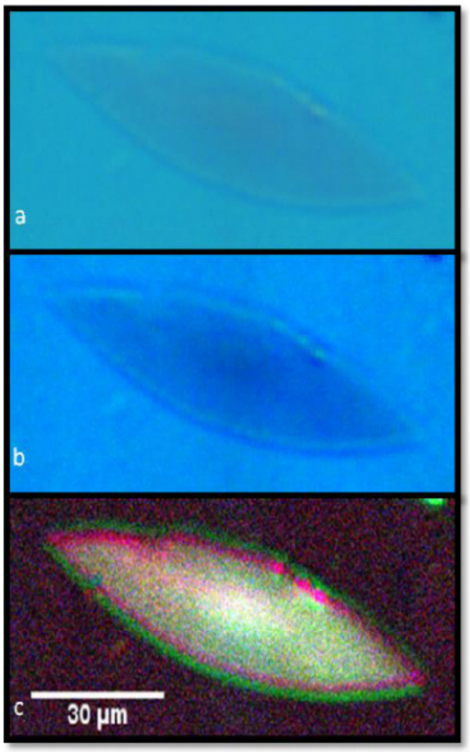
The rising applications of enriched unsaturated fatty acid fractions are significantly increasing the need for a cheap method of manufacturing such fractions. Melt crystallization is an established method for purification and enrichment of desired fractions from mixtures [1, 2, 3]. Enrichment of such natural unsaturated fractions by melt crystallization processes has already been proved effective in prior investigations [1, 2]. Since then many analytical and investigative methods have been applied on various natural plant oil based poly-unsaturated fatty acid (PUFA) mixtures to generate the much needed fundamental melt crystallization data [1]. One such method is the use of in-situ polarized light microscopy [1, 4, 5].



a.Original picture from microscope camera setup
b.Picture enhanced by contrast
c.Picture enhanced by subtracting the background information and adjusting pixel intensity

Some of the important parameters affecting the melt crystallization of PUFA mixtures are nucleation and crystal growth rate. To be able to observe and visualize these micro-scale phenomena, circular polarized transmitted light microscopy was applied. A tempered chamber (Linkam LS 120) containing the sample between two object slides was placed right within the microscope camera setup (Leica DM RME and Leica DFC 500) with a viewing window. With respect to the transmitted light, the sample was placed between two circular polarized filters such that the system is calibrated for optimal visualization. Unlike linear polarization, in this method every crystal independent of its alignment in the sample, delivers an interference color different from its background. This way, the entire crystal structure could be clearly separated from the melt.

Nucleation and crystal growth rate of a high oleic sunflower oil based PUFA was measured using this method at 5K supercooling and 10K/min cooling rate. Growth curves for total crystal area and number of crystals were analyzed and illustrated graphically. A typical S-curve is observed for both the cases starting with a lag phase followed by an exponential growth phase and ending in a saturation phase.

P24

1,2,4-Triazoline-3,5-dione (TAD) chemistry for post-functionalization of the unsaturated renewable polymers

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Recently, linear, branched and cross-linked plant oil-derived polymers have attracted great interest among polymer chemists, evidenced by the increasing number of research publications as well as reviews[1]. Those polymers are shown to be good candidates for substitution of some of the platform plastics because of the fact that fatty acids readily consist of long linear aliphatic chains[2]. However, the chemical pathways applied to synthesize plastics rely on the only available reactive groups that are carboxylic acids and/or double bonds, which result in a limitation of the corresponding post-functionalization.

The first post-polymerization modification, also known as polymer analogous modification, date back to the mid-19th century with the transformation of natural rubber into a rubbery material by a sulfur treatment reported independently by Hancock and Ludersdorf and the butadiene polymer functionalization via radical thiol-ene addition reported by Serniuk et al [3]. Since then, a number of chemistries have been applied in order to introduce either chemically useful functional groups and/or to improve mechanical properties of the parent polymer analogues. On one hand, though, the revival of the thiol-ene addition reaction (both radical and Michael type) in the last decade made it very popular and hence it became a well-known tool for post-modifications. Nevertheless, this reaction still suffers from lower reactivity against non-activated / internal double bonds, which is the usual case for fat & oil- derived polymers, and is limited to the use of 10-undecenoic acid – a building block from castor oil[4]. On the other hand, thanks to the advanced performance of new catalysts, olefin metathesis reactions have successfully been applied to synthesize diverse plant oil-derived linear and branched unsaturated polymers[1]. However, an efficient post-functionalization of the polymers synthesized therefrom remained challenging.

In the present work, we would like to revisit an efficient and catalyst-free chemistry, namely 1,2,4-triazoline-3,5-dione (TAD) chemistry, for the modification and crosslinking of fatty acid-derived polymers to achieve novel renewable polymers with complex macromolecular structures that are not yet easily achievable by any currently known chemical pathway. Within this contribution, the very first examples of the application of TAD chemistries to the well-known renewable ADMET polymers as well as triglycerides will be reported and compared to thiol-ene addition reactions. TAD chemistry overcomes the drawbacks of the thiol-ene addition reactions, and thus appears to be a perfect and powerful complementary tool, enabling the access to new polymers and broadening the synthesis and/or functionalization of fatty acids and fatty acid derived (co-)polymers.

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P25

Oleochemistry at KU Leuven: a catalytic view

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Vegetable oils are used for various applications, both in food and industrial products. Although different vegetable oils with various chemical compositions are available in nature, catalytic modification is necessary to enlarge their usage possibilities and to anticipate on the fluctuating oil production numbers and oil prices. With the use of a selective heterogeneous catalyst and the appropriate process conditions, the chemical and physical properties of vegetable oils can be tuned to ensure a constant supply of a large range of different oil and fat based products for various uses.

This contribution concentrates on recent catalytic advances realized in our centre, concerning the conjugation of linoleic acid and vegetable oils[1][2], the isomerization of terpenes[2] , the partial hydrogenation of vegetable oils[3], and the synthesis of wax esters from oleochemicals. Emphasis will be on the influence of the catalyst properties on the obtained product distribution. It will be illustrated that by means of accurate catalyst design, the selectivity of the reaction can be tuned towards the intended products.

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P26

Novel terpene based bifunctional monomers for biopolymer production

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Biopolymers, as an alternative to petroleum based polymers, provide a low environmental footprint based on renewable resources. In recent years, the attention towards biopolymer production by microbes with the application of genetic engineering tools has increased drastically. Since terpenes accumulate in high amounts by diverse industrial processes, they are an ideal starting point for the production of monomers for biopolymer manufacturing. In this project a genetically modified P.putida strain containing a monooxygenase complex of P450cam was developed. This strain possesses the ability to introduce a second hydroxyl group regio-selectively at the non-activated C5 position of borneol. Using analytical techniques, addition of the hydroxyl group at the 5-exo position was confirmed. A whole cell biotransformation process at lab scale was developed for the production of the borneol compound. Therefore, three different methods were investigated: cell immobilization, two-phase system and biotransformation with cell recycling. The most promising process was determined by evaluating volumetric productivity, handling, and equipment requirements. Further studies relating to the suitability of hydroxyborneol as a monomer for the production of polymeric materials are proceeding.

P27

Transition-Metal Catalyzed Polymerization of Novel Biogeneous Monomers

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With more than 260 Mt per year polymers are the major products of chemical industries.[1] Their application is that all-encompassing that we literally live in the 'age of plastic'.[2] Functionalized polymers not only show special properties on their own, moreover they can be used to form graft or cross linked polymers.[3] Though there is a big interest in the use of sustainable sources for polymer synthesis, the main amount is still produced from fossil resources.[4] We are synthesizing new monomers based on plant oils, itaconic acid and alcohols derived from cellulose, lignin and other sustainable sources. Unsaturated fatty acid derivatives can be applied in olefin polymerization reactions. Itaconic acid with its two acid groups gives rise to a broad variety of monomers.[5] Esterfication with methanol, fatty alcohols, or aromatic, lignin based alcohols leads to various mixed and symmetrical diester compounds which not only constitute environmentally benign alternatives for hazardous acrylates but also offer a comfortable way for a variation of the polymers properties. These monomers are then subjected to transition metal catalyzed copolymerization reactions and the properties of the resulting polymers are analyzed. A main objective herein is the direct polymerization of plant oils like high oleic sunflower oil and high erucic rapeseed oil and their derivatives like unsaturated esters and alcohols. The challenge in polymerizing these substrates is the internal cis configured double bond which needs to be activated for polymerization. Current approaches to overcome this problem use metathesis reactions to either form a substrate with a terminal double bond by reaction with ethylene or a symmetrical diester compound from homo metathesis.[6] Our approach to address this problem is the combination of an isomerization of the double bond with the polymerization reaction. In this case, terminal or maybe as well trans olefins could be polymerized with established polymerization methods.[7] The project will thus contribute to the utilization of renewable resources – first of all plant oils but also itaconic acid and its derivatives – for the production of high value added polymers.

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P28

$[Pd(\mu\text{-}Br)P(tBu)_3]_2$: A Highly Active Isomerization Catalyst for Unsaturated Compounds

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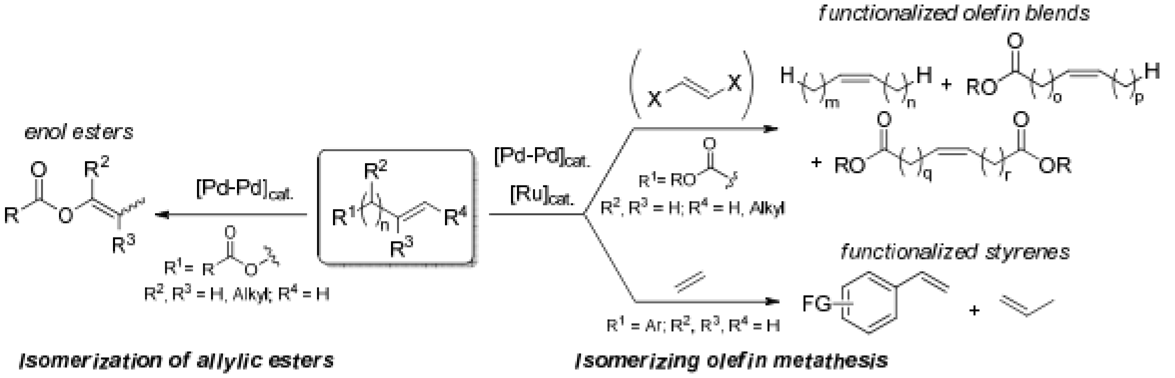
The binuclear Pd(I)-complex $[Pd(\mu\text{-}Br)(P^tBu_3)]_2$ was found to be highly active for catalyzing double-bond migration in unsaturated substrates under mild conditions. It shows a broad applicability in the isomerization of a range of allylic compounds such as allylic ethers, alcohols, amides, and arenes. Even allylic esters were efficiently converted into enol esters, rather than the catalyst inserting into the allylic C–O-bond.[1] This transformation is unprecedented for palladium catalysts and is mediated by Ru- and Fe-complexes only at much higher loadings and temperatures.[2]



Furthermore the Pd(I)-dimer shows a high tolerance towards other catalyst systems such as metathesis catalysts, which makes this isomerization catalyst versatile for cooperative reactions. In this context, we investigated the application of isomerizing olefin metathesis to convert unsaturated fatty acids into defined olefin blends.[3] The proof of concept was achieved for the isomerizing self-metathesis, cross-metathesis, and ethenolysis. With this strategy, olefin blends with tailored chain length distributions become available from renewable resources rather than from crude oil.
Another application of this concept is the isomerizing ethenolysis of alkenylarenes. When these olefins were treated with a Pd-/Ru-based catalyst system under ethylene pressure, they were cleanly converted into the corresponding styrenes along with the volatile byproduct propylene.

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P29

Process optimization of biotransformation based bifunctional monomer generation via Candida tropicalis

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Up to now, most of the existing polymeric materials are made from fossil based resources. In times of rising oil prices and scarcity of resources it is important to find alternatives for favorable plastic monomers based on renewables. One strategy to obtain bifunctional monomers from fatty acid based feedstock is the selective biotransformation by yeast such as Candida tropicalis. Cell based biotransformation processes can be divided into two stages, the growth and the biotransformation phase. To characterize and optimize the influence of different process parameters we use a DASGIP eightfold parallel fermenter system. To ensure comparability of the various approaches, it is essential to obtain the same amount of biomass used for biotransformation. We observed a wide variation of the optical density and bio dry mass under identical cultivation conditions in the growth phase. Microscopic analysis of the fermentation broth showed pseudo mycelia formation of Candida tropicalis and accumulated cell debris sticking to fermenter's wall or other installations was observed by eye. This was identified as the reason for different cell densities determined in the individual bioreactors. So mechanical foam breakers and an adapted gassing strategy was used to avoid floating of the cells and to obtain reliable and comparable initial cell densities for biotransformation without the use of large amounts of anti foam.

P30

Polymerization of linseed oil via acyclic triene metathesis (ATMET)

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Plant oils are earning growing attention since these renewable and versatile materials could potentially replace petroleum derivatives materials for the synthesis of new polymers. As linseed oil mainly consists of α-linolenic acid, a carboxylic acid with an 18-carbon chain and three cis double bonds, could also be an interesting alternative for the synthesis of branched and functionalized polyesters via acyclic triene metathesis (ATMET).[1] Polymer nanoparticles of monomers with very low water solubility, such as linseed oil, can be readily obtained by miniemulsion polymerization as monomer nanodroplets act as a nanoreactors.[2] However, it is a challenge to perform metathesis reactions in miniemulsion due to two important and negative effects of metathesis catalysts, namely the partial ruthenium methylidene decomposition in water and the possible decrease of catalyst activity in miniemulsion depending on the used surfactant type.[3] In the present work, a set of ATMET polymerizations of linseed oil was performed in bulk and miniemulsion to evaluate the activity of different types of ruthenium-based catalysts (Grubbs 1st and 2nd generations, Hoveyda-Grubbs 2nd generation and Umicore M2) in both systems. Three different surfactants (Cetyltrimethylammonium bromide, Tween 80 and Lutensol AT80) were evaluated in the miniemulsion reactions. In order to achieve higher molecular weights, vacuum or nitrogen purging were used. The studied processes produced polymers with number average molecular weight (Mn) up to 6.3 kDa in bulk and 5.8 kDa in miniemulsion, depending on the catalyst and the surfactant employed. The higher molecular weights observed in the reactions in bulk may be attributed to partial Ru-benzylidene catalysts decomposition in water.[3] Moreover, Mn results were found comparable to bulk reactions when using Umicore M2 catalyst and the Lutensol AT80 surfactant in miniemulsion polymerization, indicating that this catalyst is more robust in the presence of water and that the non-ionic surfactant Lutensol AT80 does not affect the kinetics of ATMET reactions.

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ADMET and thiol-ene reactions in miniemulsion

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Fatty acids have been studied as renewable building blocks for the synthesis of compounds with high added value and specific properties. Furthermore, often only a few minor modification reactions have to be performed prior to their application. In this context, acyclic diene metathesis (ADMET) and thiol-ene reactions are promising techniques to obtain high molecular weight polymers from these renewable raw materials.[1] Polymerization reactions in aqueous miniemulsion systems enable the production of polymeric nanoparticles with unique characteristics and vast commercial interest - e.g. structured nanoparticles presenting different morphologies: hollow, hybrid, well-defined microstructure, and nanocapsules for inorganic solids or drugs encapsulation. Moreover, there is a growing interest to perform metathesis and thiol-ene reactions in an aqueous phase aiming to work with an environmentally friendly system, but only few works were reported.[2, 3] In this work, acyclic diene metathesis (ADMET) and thiol-ene polymerization reactions were successfully performed in aqueous miniemulsion and compared to bulk reactions. Different types of ruthenium-based catalysts (for metathesis reactions) and different surfactants (anionic, cationic and non-ionic) were evaluated. Moreover, it was possible to observe that the much higher surface area of the organic phase in miniemulsion polymerization improves the release of the ethylene formed during the metathesis reaction from the polymer particles if the reactions are performed without any attempt, such as vacuum or nitrogen flow, to remove the ethylene from the reaction medium.[3] The same advantage was also observed during the thiol-ene polymerizations, since the miniemulsion reactions were less affected by oxygen inhibition than the bulk reactions.

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