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

# Fats and Oils as Renewable Feedstock for the Chemical Industry

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Abstracts
List of Participants

**2. - 3. September 2007**
**Emden, Germany**

in Cooperation with:
University of Applied Sciences OOW
German Society for Fat Science (DGF)
Agency of Renewable Resources (FNR)

Deutsche Gesellschaft für Fettwissenschaft e.V.

## Scientific and Organizing Committee

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

Michael A. R. Meier, University of Applied Sciences OOW

### Acknowledgement

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# Program

# Lectures and Posters

**Sunday, 2.09.2007**

14.00 Registration

*Chair: Jürgen O. Metzger*

15.00 Welcome and opening remarks.

15.15 Joel Barrault, Laboratoire de catalyse en Chimie Organique, Poitiers, France,
**L1 "Glycerol: a renewable and valuable molecule for a sustainable chemistry"**

15.45 Klaus-Dieter Vorlop, FAL Braunschweig, Germany
**L2 "Biotransformation of glycerol to 1,3-propanediol"**

16.15 Christian V. Stevens, Department of Organic Chemistry - Center of Renewable Resources, Faculty of Bioscience Engineering, Ghent University, Ghent, Belgium
**L3 "Utilization of fatty acid derivatives in the development of bio-based chemicals"**

16.45 Ursula Biermann, University of Oldenburg, Oldenburg, Germany
**L4 "Hydroalkylation of Unsaturated Fatty Compounds"**

17.05 – 18.00 **Poster session**

19.00 Dinner at Parkhotel Upstalsboom

**Monday, 3.09.2007**

*Chair: Joel Barrault*

9.00 Matthias Beller, Leibniz-Institut für Katalyse e.V. an der Universität Rostock, Rostock, Germany
**L5 "Homogeneous catalysis: perspectives for the use of renewable feedstocks"**

9.30 U. Kragl[a,b], C. Vogl[a], E. Paetzold[a], a) Leibniz-Institute for Catalysis at the University of Rostock; b) Institute of Chemistry, University of Rostock, Rostock, Germany"
**L6 "Hydroformylation of oils in two phase systems"**

9.50 Andreas Martin, Angela Köckritz, Leibniz-Institut für Katalyse e. V., Berlin, Germany
**L7 "Epoxidation of methyl oleate by molecular oxygen"**

10.10 Matteo Guidotti, Rinaldo Psaro, Maila Sgobba, Nicoletta Ravasio, CNR-Istituto di Scienze e Tecnologie Molecolari, and Dip. Chimica IMA and INSTM - UdR Milano, Milano, Italy
**L8 "Heterogeneous catalytic processes for the selective epoxidation of unsaturated FAMEs"**

10.30 Coffee break

*Chair: Matthias Beller*

11.10 Herbert Riepl, Institute of Resource- & Energy Technology, TU München, Germany
**L9 "Olefin metathesis of fatty acids. On the way to the industrial realization"**

11.30 Michael Meier, University of Applied Sciences OOW, Emden, Germany
**L10 "Novel Monomers and polymers from plant oils"**

11.50 Walter Kaminsky, Institute for Technical and Macromolecular Chemistry, University of Hamburg, Hamburg, Germany
**L11 "New polymers by copolymerization of olefins with bio oil components"**

12.20 Lunch break

*Chair: Michael Meier*

13.40 George John, Department of Chemistry, The City College of the City University of New York
**L12 "Soft NanoMaterials from Renewable Resources: A New Paradigm"**

14.10 Cor Koning, Eindhoven University of Technology, The Netherlands
**L13 "Novel renewable polyesters for coating applications"**

14.40 Harald Häger, Degussa, Marl, Germany
**L14 "Polyamides from renewable feedstocks: new materials versus established products"**

15.10 Paul Birnbrich, Cognis, Düsseldorf, Germany
**L15 "Oxazolines, seen from an industrial perspective"**

15.30 Fabrizio Micciche, TU Delft, The Netherlands
**L16 "Environmentally Friendly Alternatives for Co-based Dries for the Drying of Alkyd Paints: A Biomimetic Approach"**

15.50 Closing remarks

16.00 End

## **Poster Session:** Sunday, September 2, 17.05 – 18.00

P1. I. Vanaga, T. Paeglis, R. Serzane, M. Strele, M. Jure, Riga Technical University, Faculty of Material Science and Applied Chemistry, Riga, Latvia
**"Compositions of Biodegradable Chain Saw Oils Based on Rape, Hemp and Sea Buckthorn Oils"**

P2. Hanan Atia[1], Udo Armbruster[2], Andreas Martin[2], 1) Faculty of Women for Science, Arts and Education, Ain Shams University, Cairo, Egypt; 2) Leibniz-Institut für Katalyse e.V. (Außenstelle Berlin), Berlin, Germany
**"Dehydration of glycerol to acrolein in gas phase using heteropolyacids as active compounds"**

P3. Yuni K. Krisnandi[1], Marek Checinski[2], Reinhard Eckelt[2], Andreas Martin[2], Manfred Richter[2], [1] Dept. Chemistry, Faculty of Math.& Science, University of Indonesia, Depok 16424 Indonesia, [2]Leibniz-Institut für Katalyse e.V. an der Univ. Rostock, Außenstelle Berlin, Berlin, Germany
**"In-depth study of glycerol etherification on Cs ion-exchanged zeolites"**

P4. Gökhan Çaylı, Selim Küsefoğlu, Boğaziçi University, Department of Chemistry, Istanbul, Turkey
**"Synthesis and Characterization of Biobased Allyl Acrylates"**

P5. Xin Jin, Roderick Bouvy, Stephen Picken, TU Delft and nabasco, Delft, The Netherlands
**"Polyester from natural sources"**

P6. Anastasiya Rybak, Michael A. R. Meier, University of Applied Sciences OOW, Emden, Germany
**"Cross-Metathesis of Unsaturated Fatty Acid Esters"**

P7. Patrice A. Fokou, Michael A. R. Meier, University of Applied Sciences OOW, Emden, Germany
**"Polymers from renewable resources: 2-Oxazolines from plant oils"**

P8. Tina Jacobs, Marco Schubert, Michael A. R. Meier, University of Applied Sciences OOW, Emden, Germany
**"Acrylate and Methacrylate Monomers from plant oil renewable resources"**

# Abstracts

# Part 1: Lectures

**L1**

# GLYCEROL : A RENEWABLE AND VALUABLE MOLECULE FOR A SUSTAINABLE CHEMISTRY

**Joel BARRAULT**
LACCO, Laboratoire de catalyse en Chimie Organique
40, Avenue du recteur Pineau
86022 Poitiers, cédex, France.
Joel.barrault@univ-poitiers.fr

In recent papers describing the main trends of the glycerol production there is a general agreement and call for new and important efforts to find new added-values uses for glycerol. Indeed due to a large increase of biodiesel manufacture from vegetable oils the glycerol production should reach 1.5 MT in 2008 instead of 1.0 MT in 2005.

Glycerol is a multifunctional molecule which can be used for the selective synthesis of numerous products among which polyglycerols, polyglycerols esters, dissymmetric ethers, monoglycerides, glycerol carbonate, propanediols, glyceraldehyde, glyceric acid, acrolein, glycidol, … are very convenient as emulsifiers, solvents, fuels additives, tensioactive agents, monomers, intermediates, … Moreover, new molecules such as (thio-) carbamic esters are very promising as fungicides (of vegetables in biofuels production) or nucleosides analogs with antiviral activity.

In various places all around the world most of the synthesis were investigated or are under investigation using new and very selective catalysts prepared from the new concepts of solid chemistry, organometallics, hybrids and using new processes (supercritical conditions, ionic liquids, microwaves, …).

**L2**

# Biotransformation of Glycerol into 1,3-Propanediol

Klaus-Dieter Vorlop

*Bundesforschungsanstalt für Landwirtschaft, Institut für Technologie und Biosystemtechnik, Bundesallee 50, 38116 Braunschweig*

Glycerol is mainly a by-product of fat splitting and biodiesel production. Further growth of the biodiesel market would result in a fall in price of glycerol. Particularly glycerol water from RME production, for example, would be an interesting raw material, if it could be utilized in fermentation without further pretreatment. Under anaerobic conditions bacteria can transform Glycerol into 1,3-Propanediol (1,3 PD), which can be used as monomer in the chemical industry. One of the applications of 1,3-PD is use as a diol component in the plastic Polytrimethyleneterephthalate (PTT). PTT is a new polymer with properties comparable to Nylon. It is preferably used for carpets (Corterra® by Shell) or special textile fibers (Sorona® by DuPont). Additional applications are opening up in polyester resins, mainly in the paint industry.

PD can be produced biotechnologically from glycerol with the aid of bacteria. Another way would be the utilization of glucose instead of glycerol, which would provide independence from the fluctuating glycerol market.

However under certain conditions, the classic technique based on glycerol can be quite interesting with regard to technical and economic aspects: A concerted, extensive search for new microorganisms (screening) and improved process design (fed-batch with pH-controlled substrate dosage) allowed the product concentrations, which were relatively low at a maximum of 70 to 80 g/L as a result of product inhibition, to be raised to more than 100 g/L. An additional advantage of the new technique and the new isolated strains is the utilization of low-priced crude glycerol or glycerol-water. This is a factor which should not be underestimated and has a direct effect on the product costs. Further on, the use of immobilized cells compared to freely suspended cells enables an increase of productivity from about 2 up to 30 g PD/(L·h).

A comparison of existing (chemical) techniques with the new biotechnical techniques based on different substrates and glycerol qualities (= raw glycerol costs) shows that biotechnology might be competitive to chemical techniques if crude glycerol is used.

The author like to thank FNR (Agency of Renewable Resources, FKZ 22006798), and the EU (BioDiol QLK5-CT-2002-01343) for financial support.

Hirschmann S, Baganz K, Koschik I, Vorlop K-D (2005) Development of an integrated bioconversion process for the production of 1,3-propanediol from raw glycerol waters. *Landbauforsch Völkenrode* 55(4):261-267.

## L3

# Utilization of fatty acid derivatives in the development of bio-based chemicals

Christian V. Stevens
*Department of Organic Chemistry - Center of Renewable Resources, Faculty of Bioscience Engineering, Ghent University, Coupure Links 653, B-9000 Ghent, Belgium.*
*E-mail: Chris.Stevens@UGent.be*

In the last decade, renewable resources are getting more attention in view of their positive effects on the sustainability of processes, the reduction of greenhouse gas emissions and the opportunities to develop biofuels. Especially, the research and the production of bio-ethanol and biodiesel is the major topic when talking about renewables. However, the production of biomaterials and bio-based building blocks for the chemical industry, which will be the major challenge in the long run, is getting much less attention. Therefore, it is essential to invest in studying the production of bio-materials and building blocks for the future in a multidisciplinary way.

The SynBioC (Synthesis and Bioresources Chemistry) group is recently engaged in the production of bio-based building blocks from castor oil. Undecenoic acid can be readily obtained by a thermal treatment under vacuum of ricinoleic acid, which composes 85-95 % of the castor oil. Undecenoic acid has been dimerised by an acyloin condensation to a polyfunctional building block of which the reactivity and usefulness is now being evaluated. The C22-building block has been transformed into a C-20 tetrachlorodiacid which is used as a building block for the synthesis of the aminopeptidase inhibitor Tyromycin A. The synthesis of the bio-based building blocks on route to Tyromycin A will be discussed.

Further work in our group has been focused on the chemistry of inulin. Inulin, the polydisperse reserve polysaccharide from chicory, has been modified by carbamoylation and esterification in organic solvents to develop a variety of modified inulin derivatives from which the interfacial and emulsion stabilizing properties were determined. The medium and long chain acylated/carbamoylated inulin derivatives, with low degrees of substitution (DS), showed a good to very good reduction of the interfacial tension which makes these biopolymers interesting in the field of biodegradable emulsifying agents. Inutec SP1 has been developed in collaboration with industry as a new and high performing emulsifying agent for the cosmetic industry, as well as for the latex industry.

L4

# Hydroalkylation of Unsaturated Fatty Compounds

Ursula Biermann,* Jürgen O. Metzger
*University of Oldenburg, Oldenburg, Germany*
ursula.biermann@uni-oldenburg.de

The alkylation of long-chain unsaturated fatty compounds is of great importance because alkyl branched oleochemicals have interesting properties. They are used for many applications such as lubricants, cosmetics, softeners, defoamers and wood-protecting agents. The ethylaluminum sesquichloride ($Et_3Al_2Cl_3$)-induced Friedel-Crafts alkylation using alkyl chloroformates is a new method for the hydro-alkylation of unsaturated fatty compounds.[1] The reaction of e.g. oleic acid with isopropyl chloroformate gave, mediated by $Et_3Al_2Cl_3$, after a reaction time of 2h, an approximately 1:1 mixture of the regioisomers 9- and 10-isopropyloctadecanoic acid in a yield of 72%. In the presence of $Et_3Al_2Cl_3$ isopropyl chloroformate decomposes by formation of $CO_2$ and the isopropyl cation, which adds to the C,C-double bond of the fatty acid. Transfer of a hydride ion from $Et_3Al_2Cl_3$ to the adduct carbenium ion gives the saturated product. In some cases as, e.g., in hydro-alkylations of 10-undecenoic acid addition of a hydride donor such as triethylsilane was necessary. With respect to the wide spectrum of applications for alkyl-branched fatty compounds, it should be of interest to find more simple reaction conditions to perform the hydroalkylation.

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**L5**

# Homogeneous Catalysis: Pespectives for the Use of Renewable Feedstocks

Matthias Beller
Leibniz-Institut für Katalyse e.V. an der Universität Rostock, Albert-Einstein-Str. 29a,
18059 Rostock, Germany.
Matthias.beller@catalysis.de ; Fax 49 381 12815000

More than 80% of all products of the chemical industry are made via catalysis. In this regard catalysis is a key factor for achieving a sustainable production of chemicals today and in the future. In the talk it will be shown that molecular-defined palladium, copper, and iron catalysts enable chemists to perform their organic syntheses more selectively and with improved economics. Examples for the catalytic conversion of renewable feedstocks will be given. Starting from our work in hydrogenations[1] and oxidation reactions[2] as well as modern CC-coupling reactions[3] the challenges for a change from fossil resources to renewables will be discussed.

1. S. Enthaler, G. Erre, M. K. Tse, K. Junge, M. Beller, *Tetrahedron Lett.* **2006**, *47*, 8095-8099.
2. M. K. Tse, C. Döbler, S. Bhor, M. Klawonn, W. Mägerlein, H. Hugl, M. Beller, *Angew. Chem.* **2004**, *116*, 5367-5372; *Angew. Chem. Int. Ed.* **2004**, *43*, 5255-5260; b) G. Anilkumar, B. Bitterlich, F. Gadissa Gelalcha, M. K. Tse, M. Beller, *Chem. Commun*. **2007**, 289-291.
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## L6

# Hydroformylation of oils in two phase systems

*U. Kragl a, b, C. Vogl a, E. Paetzold a,*
a Leibniz-Institute for Catalysis at the University of Rostock, Rostock, Germany
b Institute of Chemistry, University of Rostock, Rostock, Germany

**Introduction:**

During the last few years the hydroformylation or oxo-reaction of unsatured fatty acid derivatives [1] has become an interesting field of research, for both, academia and industry [2, 3]. Up to now no reaction system was found which achieves good yields and allows catalyst recycling as well. According to this no industrial process has been developed. Here ionic liquids present a new, promising approach [4]. As reported in literature before, the recycling of the catalyst is very simple.

**Aim:**

The Aim of our work is the hydroformylation of methyl oleate and other unsatured fatty acid derivatives. The subsequent reaction of the obtained aldehyde to e.g. alcohols, esters or carbon acids leads to an interesting and manifold range of products. The use of ionic liquids will lead to a multi-phase reaction system, in which the recycling of the catalysts phase is performed easily and quantitatively. Ionic liquids based on quaternary ammonium compounds, which are in use here, are available on large scale at low costs and they are fully tested due to toxicological properties.

**Results:**

With a simple catalyst system a conversion up to 98% with selectivity up to 100% were reached within short reaction times under moderate conditions (120 °C, 70 bar syngas pressure). The product was identified as pure aldehyde[5]. The simple separation of product and catalyst phase leads to a novel reaction engineering. The catalyst phase was recycled several times, the leaching was outstanding low.

**Literature:**

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[5] C. Vogl, unpublished results.

## L7

# Epoxidation of methyl oleate by molecular oxygen

Andreas Martin, Angela Köckritz

*Leibniz-Institut für Katalyse e.V. an der Universität Rostock, Außenstelle Berlin, Richard-Willstätter-Str. 12, D-12489 Berlin*

Epoxides of triglycerides and derivatives of fatty acids are industrially synthesized via peroxo acids, in general. The products are valuable chemicals for manufacture of a good number of plasticizers, reactive diluents and stabilizers. However, sustainable chemistry might prefer the use of molecular oxygen as green oxidant. Besides the use of metal-containing oxidation catalysts, some decades ago Swern [1] described an oxidant-reductant system ($O_2$-aldehyde) for epoxidations of double bonds for the first time. Current applications and developments are reported for example by Nagata et al. [2] and Kureshi et al. [3]. Reactant conversion and product yield are dependent on the aldehyde structure, branched aliphatic aldehydes (e.g. isobutyric aldehyde) showed best results. The use of metal catalysts in this reaction seems to increase product selectivity besides their impact on oxygen activation [2,4].

An extensive screening of various oxidation catalysts (Co, Cu, Fe salts) in epoxidation of methyl oleate using $O_2$ revealed best activities and yields for cobalt halogenides in the presence of modifiers such as ammonium bromide. The tests were carried out at 90 °C and 4 bar oxygen pressure in batch autoclaves using dichloroethane as solvent. At almost complete conversion product selectivity raised up to ca. 50-55 %, by-products were some other oxygen-containing monomers and/or polymers such as 9- or 10-oxocompounds.

Besides, the epoxidation was also studied in presence of aldehydes and radical initiators (e.g. AIBN) in aqueous as well as organic reaction systems without metal-containing catalysts. Surprisingly, much better activities and product yield were obtained. Straight-chained aldehydes are superior to branched compounds dominating the reaction in aqueous reaction system, at 90 % conversion ca. 80 % epoxide are formed (80 °C, 1 bar $O_2$). Isobutyric aldehyde as well as hexanal showed best results in organic solvent reaction system (e.g. dichloroethane) with more than 90 % yield at complete conversion (70 °C, 4 bar $O_2$). Furthermore, effect of reaction time, solvent and nature of applied aldehyde was studied.

The authors like to thank FNR (Agency of Renewable Resources, FKZ 22003704) for financial support, HOBUM Oleochemicals for cooperation and Mrs. S. Ziemann for experimental assistance.

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[3] R.I. Kureshi, N.H. Khan, S.H.R. Abdi, P. Iyer, J. Mol. Catal. A: Chem. 124 (1997) 91.
[4] M.G. Clerici, P. Ingallina, Catal. Today 41 (1998) 351.

**L8**

# Heterogeneous Catalytic Processes for the Selective Epoxidation of Unsaturated FAMEs

*Matteo Guidotti*, Rinaldo Psaro, Maila Sgobba, Nicoletta Ravasio*
CNR-Istituto di Scienze e Tecnologie Molecolari, via G. Venezian 21, MILANO, Italy
Dip. Chimica IMA and INSTM - UdR Milano, via G. Venezian 21, MILANO, Italy

Epoxidised fatty acid derived from vegetable sources can be used in several domains (*e.g.* plasticisers in polymers, additives in lubricants and components in plastics)[1,2]. More environmentally friendly synthetic routes than the nasty conventional stoichiometric peroxyacid process are desirable and the use of heterogeneous titanium catalysts shows to be a viable, sustainable and acid-free method to epoxidise selectively fatty acid methyl esters (FAMEs) derived from vegetable fats and oils[3]. The titanium-containing solids are obtained by grafting titanocene dichloride ($TiCp_2Cl_2$) onto silicas of various morphologies: ordered or non-ordered mesoporous materials, pyrogenic silica or commercial mixed oxides (Ti loading *ca*. 1.8 wt.%). Pure FAMEs and mixtures of methyl esters directly obtained (with $NaOCH_3$) from samples of commercial plant oils, such as high-oleic sunflower, coriander, castor, soybean or vernonia oils are thus converted into the related epoxides under acid-free conditions using *tert*-butylhydroperoxide (TBHP) as oxidant.

The mixtures, naturally rich in one fatty acid (high-oleic sunflower in **1**, soybean in **2**, castor in **3**, coriander in **4** and vernonia in **5**), are taken as models to study how the position of the unsaturations and the substituents on the FAME hydrocarbon chain affect the catalytic performance[4].

Along with interesting catalytic results (Table 1), the physico-chemical characteristics of the environment surrounding the Ti sites (morphology, hydrophobic/hydrophilic character, etc.) plays a relevant role in influencing the activity and selectivity of the catalyst. The Ti-MCM-41 catalyst displays globally better performance in terms of activity than the non-ordered ones and this is explained by a better exposition and dispersion of Ti(IV) sites over Ti-MCM-41 than over other lower surface-area supports. Over a di-unsaturated FAME (as methyl linoleate **2**) Ti-MCM-41 is sufficiently active to lead to the formation of reasonable amounts of methyl diepoxystearate, whereas, over other Ti-$SiO_2$ catalysts, the monoepoxidised derivative is the major product after 24 h. These high activity and selectivity are ascribed to the highly hydrophilic character of the surface of Ti-MCM-41, which can increase the residence time of the intermediate monoepoxide, thus enhancing the formation of diepoxide. In fact, the removal of the surface silanols (by modification with silylating agents) causes a remarkable loss in selectivity towards diepoxides, confirming that a hydrophilic environment around the titanium active sites has often a beneficial effect in the epoxidation of richly functionalised substrates[5]. Promising results are also obtained under solvent-free conditions and the catalysts are easily recovered and recycled.

Table 1. Catalytic performance of Ti-catalysts with pure FAMEs

| Catalyst | Substrate | C (%)$^a$ | TOF ($h^{-1}$)$^b$ | $S_{monoepox}$ (%)$^c$ | $S_{diepox}$ (%)$^c$ |
|---|---|---|---|---|---|
| Ti MCM-41 | **1** | 100 | 54 | >95$^d$ | - |
| Ti MCM-41 | **2** | 94 | 38 | 28$^e$ | 72 |
| Ti MCM-41 | **5** | 92 | 34 | - | >95 |
| Ti $SiO_2$ | **1** | 92 | 16 | >95$^d$ | |
| Ti $SiO_2$ | **2** | 61 | 14 | 61$^e$ | 39 |
| Ti $SiO_2$ | **5** | 88 | 15 | | >95 |

$^a$Conversion after 24 h; $^b$TOF after 1 h; $^c$Selectivity to 1,2-epoxide after 24 h;
$^d$monoepoxystearate; $^e$monoepoxyoleate. Conditions: batch reactor; AcOEt solv.; 363 K; TBHP/unsaturation = 1.10

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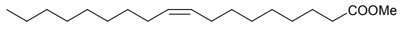

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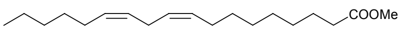

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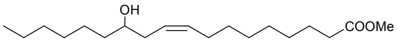

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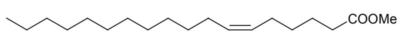

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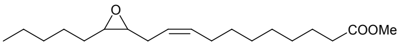

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## L9

# Olefin Metathesis of Fatty Acids: On the Way to Industrial Realization

Herbert Riepl
Institute of Resource- & Energy Technology, Technical University of Munich
h.riepl@wz-straubing.de

Olefinmetathesis is a transition metal catalyzed reaction of olefinic double bonds, whereby a formal exchange of substituents occurs. According to a suggestion originally made by Chauvin the reaction mechanism is not an exchange of substituents but a complete break and reformation of the olefinic bond with metal-carbene complexes as catalytically active intermediates. Quite different transition metal carbene complexes are able to catalyse this reaction and some technical processes based on tungsten, molybdenum or rhenium have been designed. In the last decade a huge progress has been made in the metathesis chemistry by ruthenium[1]. The first consideration of unsaturated fatty acids as source of double bonds and useful chemicals with carbon chains of intermediate carbonatom number has been made by Boelhouwer[2]. Using tungsten halides, he established the basic chemistry of the fatty acid metathesis but with low performance. Olefinic chemistry of the double bond in unsaturated fatty acids has been confined since mainly to epoxidation chemistry up to now, because the usual metal carben catalyst precursors are highly reactive towards the carboxy function, with the notable exception of rhenium[3]. Oleochemistry is confronted with the peculiarity of high boiling points of its educts and products making necessary high vacuum distillations for all components. The design of a cheap technical process of fatty acids metathesis is thus connected with establishing a catalyst of high tolerability towards oxygen, water and other common impurities of technical grade oils. Ruthenium carbene complexes with increased tolerability towards impurities are based on the exchange of the usually applied organo phoshanes with N-heterocyclic imidazolylidenes as ligands originally invented by Herrmann and Nolan[4]. High reactivity and turnover numbers are neglected in favour of stability and insensitivity. The potential is exemplified on a kg-scale process of oleic acid metathesis for synthesis of intermediates to be used in the synthesis of thermoplastic elastomers. Thermoplastic elastomers consist of a comonomer with increased tendency to crystallize ("hard-comonomer", e.g furandicarboxylic acid, terephtalic acid) and a "soft" comonomer, e.g a long chained diole. By application of selfmetathesis, a C18 dicarboxylic acid is produced. High selectivities are demonstrated also in the case of cross metathesis using functionalised olefins. Ethenolysis, which has been envisaged to be of technical interest because of the value of ω-decenoic acid, unfavourably is dependent on the very unstable Ruthenium-methyliden complex leading to reduced catalyst performance. Substituted olefins thus can yield much more stable secondary carbenes which drastically improves catalyst sensitivity. In addition, the often uttered possibility of complex product mixtures is not always a matter of fact. Allyl alcohol, and its esters, which out of four possible isomers selectively yields ω-undecenoic acid and undecenyl alcohol is an interesting example to study.

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## L10

# Novel Monomers and polymers from plant oils

Michael A. R. Meier

*University of Applied Sciences Oldenburg/Ostfriesland/Wilhelmshaven*
*Junior research group renewable raw materials, Faculty of Technology,*
*Constantiaplatz 4, 26723 Emden, Germany*
**E-mail: michael.meier@fh-oow.de ; Internet: http://www.meier-michael.com*

The use of renewable raw materials can significantly contribute to a sustainable development, usually interpreted as “acting responsible to meet the needs of the present without compromising the ability of future generations to meet their own needs”.[1] In ages of depleting fossil oil reserves and increasing emission of green house gases it is obvious that the utilization of renewable raw materials wherever and whenever possible is one necessary step towards a sustainable development of our future. In particular, this can perennially provide a raw material basis for daily life products and avoid a further contribution to green house effects due to $CO_2$ emission minimization. Furthermore, the utilization of renewable raw materials can (in some cases) meet other principles of green chemistry, such as a built in design for degradation or an expected lower toxicity of the resulting products.

Within this contribution, the utilization of plant oil renewable resources as raw materials for monomers and polymers will be discussed.[2] It will be shown that the synthesis of monomers as well as polymers from plant fats and oils already has some industrial application and recent developments in this field offer promising new opportunities. Moreover, new approaches of monomer as well as polymer synthesis using plant oils as starting materials will be discussed in detail. Especially cross-metathesis and other efficient catalytic reactions, the synthesis of oxazoline, acrylate or methacrylate derivatives and their subsequent controlled and living polymerization, as well as post polymerization functionalization procedures of the obtained macromolecules will have an important impact on the field in the future. Interesting examples and results of these new approaches towards defined and functional polymeric materials will be discussed in detail.

Financial support from the German Federal Ministry of Food, Agriculture and Consumer Protection and the Fachagentur Nachwachsende Rohstoffe is kindly acknowledged.

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L11

# New Polymers by Copolymerization of Olefins with Bio Oil Components

**Walter Kaminsky**

Institute for Technical and Macromolecular Chemistry
University of Hamburg, Bundesstr. 45, 20146 Hamburg, Germany
kaminsky@chemie.uni-hamburg.de

Polyolefins are growing faster than most other polymers. In 2006, more than 105 million tons of polyethylene and polypropylene are produced worldwide. Especially copolymers of ethene and α-olefins (LLDPE) increase rapidly. To have a better compatibility in blends between polyolefins and other plastics such as polyester or polyamids, there is a demand for polar substituted polyolefins. Long chained α-olefins and olefin esters and ethers can be obtained from bio oil.

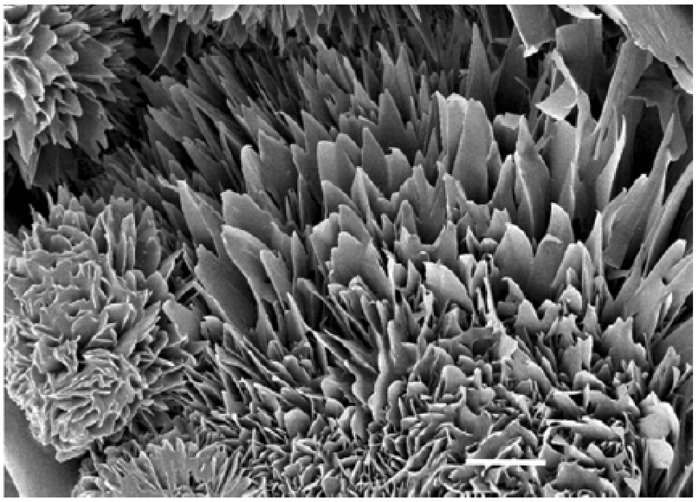
The bio oil ester (oleic acid methyl ester) can be converted by metathesis reaction in the presence of ethene into 1-decene and 9-decenoic acid methyl ester. Both components are suitable comonomers for the synthesis of polyolefin specialities by copolymerization with ethene or propene. For this copolymerization metallocene/methylaluminoxane catalyst or other single site catalysts are more active than classical Ziegler-Natta catalysts because they insert higher amounts of longer chained α-olefins or olefins with polar groups. The microstructure of these copolymers can be tailored in a great variety using metallocene complexes with different symmetries. With these catalysts it is possible to produce isotactic, syndiotactic or atactic polypropylene backbones.

By copolymerization of 1-decene from bio oil with ethene, linear low density polyethylene (LLDPE) is obtained with excellent properties. The tensile strength increases with an increasing number of carbon atoms in the comonomer. Today, 1-octene is the highest 1-olefin used because of industrial availability. This can be changed in using bio oil components. Also copolymers of ethene or propene with olefin esters or ethers from bio oil can become useful polymers.

**L12**

# Soft NanoMaterials from Renewable Resources: A New Paradigm

*George John, Department of Chemistry,*
*The City College of the City University of New York, New York, NY 10031*



The self-assembly of low molecular weight building blocks into nanoscale molecular objects has recently attracted considerable interest in terms of the bottom-up fabrication of soft nanomaterials. The building blocks currently used in supramolecular chemistry are synthesized mainly from petroleum-based starting materials. However, biobased organic synthesis presents distinct advantages for the generation of new building blocks since they are obtainable from renewable resources. Our research efforts are deeply devoted towards developing building blocks from renewable resources to generate soft materials such as new surfactants, liquid crystals, lipid nanotubes and molecular gels. Present talk illustrates few successful examples of generating self-assembled soft materials from agri-sources, through simple organic transformations and by enzyme catalysis. To take these materials to the next level, we successfully showed the utility of these hydrogels as drug delivery vehicles. Enzyme catalysis was used as a tool to make and break the hydrogels, which apparently triggered controlled drug delivery. Intriguingly, by combining biocatalysis, with principles of green and supramolecular chemistry, we developed building blocks-to-assembled materials. Also address the advances that have led to the understanding of chiral behaviour and the subsequent ability to control the structure of glycolipid nanostructures-derived from renewable resources-and the resulting impact of this on future material applications. We foresee that these results will encourage interdisciplinary collaboration between scientists in the fields of organic synthesis, materials research, surfactant science, green chemistry, drug discovery to design, and develop biobased functional materials from under-utilized plant/crop-based feedstocks, as new forms of materials, and energy needs.

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## L13

# Novel renewable polyesters for coating applications

C.E. Koning[1], B.A.J. Noordover[1], R. Duchateau[1], R.A.T.M. van Benthem[1],
J. van Haveren[2], D. van Es[2]

*[1] Technical University of Eindhoven, The Netherlands*
*[2] Agrotechnology and Food Innovations, Wageningen, The Netherlands*

Polyester resins containing terephthalic acid are widely used in powder coating industry. The monomers used in their synthesis originate from fossil feedstock. The objective of this project is the development of bio-based resins (and networks thereof) that can compete with the conventional materials with respect to mechanical properties and chemical stability. We used several renewable monomers, such as isosorbide and its isomers, affording chain rigidity to increase glass transition temperature. These dianhydrohexitols are aliphatic and are therefore expected to be less susceptible to degradation by UV radiation than the classical aromatic systems. Other sustainable monomers used in this study are adipic acid, succinic acid, tartaric acid and 1,3-propanediol. Series of clear, slightly yellow polyesters were obtained through polycondensation, with either acid or hydroxyl functionality [1]. Their glass transition temperatures strongly depend on the dianhydro-hexitol content. The $T_g$ range from 40 up to 80 ºC (with $M_n$ between 2500 and 5000 g/mol) is suitable for the envisioned application. The linear polyester resins could also be end-capped and/or modified with multifunctional monomers, affording polymer chains with enhanced functionality. In this way, network formation with commercially available curing agents was improved significantly. The different resins were subsequently used to formulate and apply coatings from solution as well as through powder coating. Initially, several classical cross-linking agents were selected in order to compare the renewable systems with conventional (powder) coatings. The coatings were cured at 200 ºC under $N_2$ flush, which led to slightly yellow transparent films with good solvent resistance, gloss, adhesion to aluminum and mechanical properties. We are currently developing sustainable curing agents to create a fully renewable system.

This project forms part of the research program of the Dutch Polymer Institute (DPI project 451).

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**L14**

# Polyamides from renewable feedstock
# – New materials versus established products –

Dr. Franz-Erich Baumann, Dr. Harald Haeger
Degussa GmbH, BU High Performance Polymers, Paul-Baumann-Strasse 1, 45764 Marl, Germany

Bio feedstock based polymers are currently under intense investigation. A lot of attention is spend on biodegradable polymers e.g. PLA. However there are current developments from DuPont towards polyesters, polyetherester and polyethers from biobased propanediol.
Those polymers are belonging clearly to the class of engineering plastics.
Polyamides based on castor oil are by far the oldest man made polymers from a renewable feedstock. Castor oil can be converted via chemical conversion to 11-Amino-undecanoic acid or decane dioic acid. The later can then be converted to decane diamine.
With those monomers polyamides like PA11 and PA1010 are available, that are completely based on renewable feedstock. Furthermore partly renewables based polyamides like PA610, PA1012, PA106, etc. are also available.
PA1010, PA610 and PA106 are belonging to the group of engineering plastics, whereas PA11 and PA1012 are true bio feedstock based high performance polymers exhibiting a unique set of properties.
These polyamides will be discussed and compared in detail and as well compared to their petrochemical counterpart PA12.
The paper will discuss the sustainability, the pathway and the properties of the above mentioned polyamides.
It is still unclear whether castor oil based polyamides or their relatives based on a petrochemical feedstock are more sustainable. The sustainability depends mainly on the monomer feedstock. One important factor are certainly the side products that castor oil based polyamide chemistry has to deal with, like glycerine or heptaldehyde.
There are some more recent developments of monomers for polyamides based on erucic acid and other unsatured fatty acids. Nevertheless all of these procedures are chemical conversions.
The synthesis of diacids from fatty acid by fermentative oxidation of the ω-methylgroups with candida tropicalis and the polyamides derived there from will also be discussed.

**L15**

# Oxazolines, seen from an industrial perspective

Paul Birnbrich
Cognis GmbH, Düsseldorf, Germany
Paul.Birnbrich@cognis.com

In 1989 a new technical production method for 2-alkyl-2-oxazolines was developed at Henkel (1, 2, 3). Starting from typical fatty-acid-ethanol-amides via condensation reaction the oxazoline-heterocycle was formed. Different titanium compounds were used as catalysts. The described synthesis was up scaled to a volume of several metric tons and oxazolines become industrial available products at that time.
A lot of research activities about oxazolines started in those years. One main focus of the investigation was the well known living cationic polymerization (4-7) of the oxazolines. Another objective was the development of oxazolines and poly(oxazolines) which could be used as blend-compatibilizer in plastics (8 -11). The use of poly-(oxazolines) for coating applications was also investigated (12-14). Beside those internal research activities, collaborations with universities and institutes started in 1990. These collaborations initiate research activities especially at universities which last until today (15-17). Now, after nearly 20 years it is time for a short review about oxazoline chemistry from an industrial perspective.

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## L16

# A Bio-inspired Iron-based Catalyst as a Promising Drier for Alkyd-based Paints

*Fabrizio Miccichè*[a,b], *Jacco van Haveren*[a], *Weihua Ming*[b], *Eef Oostveen*[a] *Rob van der Linde*[b]

[a] *Agrotechnology and Food Innovations, Postbus 17, 6700 AA Wageningen, The Netherlands*
[b] *Technical University of Eindhoven, P.O. Box 513, 5600 MB Eindhoven, The Netherlands*

A quick drying of alkyd paints is of enormous industrial importance. Alkyd paints are complex mixtures of chemicals ranging from alkyd resins, pigments, and solvents to driers based on heavy metals. Driers, mostly based on cobalt salts (e.g. cobalt 2-ethylhexanoate) are required to accelerate the oxidative crosslinking of unsaturated fatty acids chains of alkyd resins,

In spite of their importance and wide spread use, cobalt driers are not free of disadvantages, however. Besides, loss of drying upon standing, cobalt salts have shown some potentially carcinogenic effects by animal testing raising health, environmental and safety concerns. Therefore the usage of these driers has to be reduced and the demand for Co-free coatings has already begun.

To switch to a more “green and sustainable” chemistry, iron-based catalysts seem to be very promising. In Nature, iron is the primary catalyst of a broad variety of oxidative reactions (e.g. lipid., protein and DNA oxidations) especially when in combination with reducing agents such as ascorbic acid (or vitamin C) [1]. Learning from Nature, a bio-inspired approach was used to develop environmentally friendly driers for the drying of alkyd paints. In this respect, the combination of iron salts, e.g. Fe-ethylhexanoate, together with reducing agents, vitamin C and derivatives, has proven to successfully catalyze the oxidation of simple unsaturated fatty acid as model compounds for alkyd resins [2], ethyl and methyl esters of linoleic acid, and achieve excellent total drying of commercial water and solvent borne alkyd paints formulations [3].

This research has also focused on the understanding of the mechanism used by the iron-based catalyst to initiate the oxidation of ethyl and methyl linoleate by means of several analytical and spectroscopical techniques [4]. A catalytic mechanism was proposed [4].

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# Abstracts

# Part 2: Posters

**P1**

# COMPOSITIONS OF BIODEGRADABLE CHAIN SAW OILS BASED ON RAPE, FLAX, HEMP AND SEA BUCKTHORN OILS

I. Vanaga, T. Paeglis, R. Serzane, M. Strele, M. Jure
Riga Technical University, Faculty of Material Science and Applied Chemistry
vilony@gmail.com

Chain saw oils are total loss lubricants and usually are based on mineral oils. The felling of approximately 10 million $m^3$ of wood consumes about 2 million litres of chain saw oils - it causes essential pollution of soil. In the last few years a considerable attention has been devoted to biodegradable lubricants obtained from renewable resources, which do not pollute the environment. Different plant oils (e.g., soybean, rapeseed, sunflower, palm oils) are successfully used as raw materials for such lubricants. Most of the European countries (e.g., Germany, Austria) already use mainly/only biodegradable chain saw oils. Completely different is situation in Latvia: high prices of imported biodegradable chain saw oils and absence of corresponding legislation are the main reasons of continuing use of mineral oils in timber harvesting.

The main oil plants grown in Latvia are rape, flax and industrial hemp; according to the oil producers hempseed oil is the cheapest one due to the contentment and productivity of hemp. Our investigations were devoted to elaboration of compositions and production technology of biodegradable chain saw oils based on locally produced plant oils.

We used rapeseed, linseed, hempseed as well as waste sea-buckthorn oil as base fluids for our compositions. Sea-buckthorn oil was obtained from residue formed in juice production; berries of this plant are among the most nutritious and vitamin-rich fruits found. Oil from the pulp is highly unsaturated having 62-63% of its fatty acid composition; berries and seeds contain a lot of antioxidants (vitamin E) and significant levels of carotenoids, seeds contain 12-13% of a slow-drying oil.

In order to attain essential properties of chain saw oils we synthesized several additives: detergent, emulsifier, sulfurized rapeseed oil as antiwear additive, epoxidized and ozonized rapeseed, hempseed and linseed oils, polyhydroxy triglycerides and some estolides to improve oxidative stability, viscosity and low temperature properties of the compositions. It is well known that epoxy and polyhydroxy triglycerides and estolides have higher oxidative stability and enhanced kinematic viscosity in comparison with raw oils, besides that, polyhydroxy triglycerides demonstrate excellent emulsifying properties for oil in water emulsions. Some commercial additives have been used, too, e.g., low molecular weight polypropylene and Candelila wax, resin as viscosity modifiers and natural rubber based adhesive as tackifier.

We found out that compositions containing low molecular weight polypropylene, colophony, Candelila wax or epoxy triglycerides hardly form homogenous mixtures and often stratify; more stable formulations were obtained when additives were polyhydroxy triglycerides and ozonated oils. Unfortunately, mixtures containing ozonated oils have too low flash points. According to chain saw operators, one of the most essential properties for chain saw oils is tackiness; we achieved good tackiness (even better than in case of biodegradable chain saw oil of Husqvarna) by addition of natural rubber adhesive.

The best results (regarding kinematic viscosity, viscosity index, tackiness and flash point) were obtained when rapeseed oil was used as base fluid and epoxy triglycerides obtained from linseed oil and natural rubber tackifier were added. Very promising from technical, ecological and economical points of view seems application of waste sea-buckthorn oil as base oil – in this case only addition of natural rubber tackifier was necessary.

Some of our best compositions now are being tested by chain saw operators in timber harvesting.

**P2**

# Dehydration of glycerol to acrolein in gas phase using heteropolyacids as active compounds

Hanan Atia[1], Udo Armbruster[2], Andreas Martin[2]*
[1] Faculty of Women for Science, Arts and Education, Ain Shams University, Cairo, Egypt
[2] Leibniz-Institut für Katalyse e.V. (Außenstelle Berlin), Berlin, Germany

The growing production of biodiesel by transesterification of plant oil with methanol leads to a surplus production of glycerol [1]. Consequently, glycerol might be a cheap reactant for chemical syntheses. Some recent work is known from the literature, besides synthesis of propanediols or various oxidation reactions leading to ketones or acids, also formation of acrolein is described. For example, in liquid phase glycerol has been decomposed in supercritical water to yield acetaldehyde, methanol, propanal and acrolein with 84 % selectivity for acrolein at 40 % conversion using an acid homogeneous catalyst (5mM $H_2SO_4$) at 350 °C and 34.5 MPa [2]. The reaction has also been studied in the gas phase using silica supported silico-tungestic acid ($H_4SiW_{12}O_{40} \cdot 24H_2O$ = HSiW) to give a selectivity for acrolein >85 % at complete conversion at 275 °C [3]. The aim of our study was to investigate the dehydration of glycerol in the gas phase and to compare catalytic behavior of different heteropolyacids (HPA) and supports.

20 wt% of various HPAs ($H_3PW_{12}O_{40} \cdot nH_2O$ = HPW, $H_4SiW_{12}O_{40} \cdot 24H_2O$ = HSiW, $H_3PMo_{12}O_{40} \cdot nH_2O$ = HPMo, $(NH_4)_3PMo_{12}O_{40} \cdot nH_2O$ = $NH_4PMo$) have been supported over alumina with medium pore radius of 2.3 nm or silica with small pore radius of 0.8 nm to yield catalysts with different surface chemical properties. Supported HPAs were prepared by incipient wetness impregnation and then calcined at 400 °C. The materials were characterized using XRD, DTA, nitrogen adsorption, TPD and Raman spectroscopy. The catalytic tests were carried out in the temperature range of 225-300 °C using a flow system with glass tube reactor under atmospheric pressure.

In DTA measurements silica supported catalysts exhibit exothermic peak at higher temperatures than for unsupported HPAs, indicating that the Keggin structure of HPA on silica is maintained. In contrast, alumina supported solids don’t show such peaks; this is probably due to higher dispersion of HPA or due to the interaction of alumina with the HPA. XRD showed that the alumina supported material is X-ray amorphous or highly dispersed in contrast to silica supported HPA. These results have been confirmed by Raman spectroscopy which proofed that the Keggin anion has been maintained over silica.

The HSiW heteropolyacid supported over alumina showed the highest acrolein selectivity of 63 % at complete conversion at 275 °C while non-supported as well as silica supported heteropolyacids tend to decompose and to deactivate rapidly above 275 °C. The HSiW catalyst has been studied with the change of residence time and it shows even higher selectivity up to 75 % at 300 °C and a contact time of 0.13 seconds. Nevertheless, there was some deactivation after three days of repeated tests. Besides acidity, this result might be as well influenced by different porosity of the catalysts too. Surprisingly and in contrast to literature data, the chosen alumina material seems to be superior to silica as support material with regard to catalyst activity and selectivity.

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## P3

# In-depth study of glycerol etherification on Cs ion-exchanged zeolites

Yuni K. Krisnandi[1], Marek Checinski[2], Reinhard Eckelt[2], Andreas Martin[2], Manfred Richter[2]

[1] Dept. Chemistry, Faculty of Math.& Science, University of Indonesia, Depok 16424 Indonesia,
[2] Leibniz-Institut für Katalyse e.V. an der Universität Rostock, Außenstelle Berlin,
Richard-Willstätter-Str. 12, D-12489 Berlin

Glycerol is an abundant by-product of biodiesel production, and, hence, its conversion to attractive consumer products like diglycerol is desirable. Cesium modified solids are reported [1] to be a promising catalyst class for glycerol etherification, but the role and fate of cesium during reaction is still under discussion. The present work centers on the influence of the zeolite structure on the catalytic properties of Cs ion-exchanged samples with focus on diglycerol distribution and factors that govern formation of these target products. The work benefits from preceding reports of Barrault et al. [2,3].

Commercial zeolite samples of MFI, BEA, FAU structure type were used for ion exchange with 0.4 M of $CsNO_3$ or Cs-acetate solution (0.02 g zeolite/ml solution, 60 °C, 24 h, under stirring). Characterization of the solids comprised XRD, XRF, SEM, $N_2$ adsorption and thermal analysis. Glycerol etherification was carried out in glass-reactor equipped with a mechanical stirrer in the presence of 2 wt.% of catalyst. Water formed during reaction was evaporated and condensed. The reaction was performed at 260 °C for 8 and 24 h, respectively, with 50 g of glycerol under Ar flushing of 50 ml/min. Reagents and products were analyzed after silylation [4] by GC. Details will be given elsewhere [5]. DFT-calculations (6-311(2d2p)/B3LYP) were performed on neutral and anionic conformational glycerol and diglycerol isomers to understand experimentally observed isomer distributions.

Activity (glycerol conversion after 8 h reaction time) was found to be in the order of Cs-X > Cs-Y > Cs-USY > Cs-beta > Cs-ZSM-5 with 63 % and 5 % conversion over Cs-X and Cs-ZSM-5, respectively. XRD and SEM analysis of spent catalysts proved that the Cs-Y and Cs-X zeolites suffered a structural collapse during reaction (most severe for Cs-X) with release of Cs into solution (as confirmed by XRF). This explains why the activity found for Cs-X resembled that of the homogenous $CsHCO_3$ catalyst, characterized by a high percentage of glycerol trimers and tetramers. The exceptional activity of Cs-X reported in the literature is obviously associated with the observed structural instability and the release of Cs. This conclusion was corroborated by results obtained for the more stable Cs-Y, where practically no trimers or tetramers were found after comparable reaction time. A shift of diglycerol distribution in favor of the $\alpha\beta$-isomer was observed over Cs-Y.

DFT calculations showed that the energetically most favored anionic glycerol conformation resulted after charge location at the middle oxygen. A nucleophilic attack to a $CH_2OH$ group of a second glycerol leads to $\alpha\beta$-diglycerol. On the other hand, the calculations on dimers and their anions shows that thermodynamic stability of dimer conformation are $\alpha\alpha' \approx \alpha\beta > \beta\beta'$, respectively.

The ongoing in-depth study on the peculiarity of cesium for catalyzing the glycerol etherification under solvent-free conditions has shown that the outstanding activity of Cs-X is due obviously to the prevailing homogenous Cs catalyzed reaction, after collapsing of the zeolite structure under reaction conditions.

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**P4**

# Synthesis and Characterization of Biobased Allyl Acrylates

Gökhan Çaylı, Selim Küsefoğlu*
Boğaziçi University Istanbul,Turkey
Department of Chemistry
* kusef@boun.edu.tr

Allyl acrylates are versatile compounds and they are used in wide variety applications from photo resist resins to dental products. Mostly, Allyl acrylates are synthesized by esterification reaction between allyl alcohols and acyl chlorides of acrylates. These acyl chlorides are very toxic and allyl alcohol is not found in nature. In this study, an easy and efficient method for synthesizing of allyl acrylates which are derived from methyl oleate is presented. There are two steps in the procedure. At the first step allylic bromides of methyl oleate is synthesized and at the second step, replacing of the bromine on the allylic positions of methyl oleate with $Na^+$ or $K^+$ salts of acrylic or methacrylic acids occurs. The yield of the reaction is around 70 % for methacrylic acid and 85% for acrylic acid. Purification of the products is done with column chromatography. The homo and copolymers of these monomers are prepared by free radical polymerization techniques.

## P5

# Polyester from natural sources

Xin Jin, Roderick Bouvy, Prof. Stephen Picken

Key words: polyester, diacid, glycerol, diol, natural sources, fermentation

### Background driving force

Along with the fast growing of composite industry, the demands for petroleum resources are also increasing sharply. A significant disadvantage of the common composite materials is their impact on the environment during production.
A bio-based product has a bio-material content of 90% or more wherein the non-bio-based content is incidental to the overall product performance and made necessary only because a bio-based equivalent does not yet competitively exist in the market place.

### Objective of the feasibility study

In this feasibility study we will look through the existing technologies on bio-based resin production and also find possible feedstocks for resin production which must be natural, environmentally friendly, biodegradable, not much(too) expensive, chemically stable, and commercially available in the market

### Researches on existing bioresin

There are existing and commercial feasible thermoset bioresins on (epoxydised) plant oil base, sugar base, lactic acid base, biobased polyols.

### Researches on diacid, diacid anhydrides, diols, glycerol cross-linking monomer natural sources

To make natural based polyester by condensation polymerisation we have done some researches on diacids, diols and glycerol with natural sources. For diacid and diacid anhydrides, we did researches on the availability, feedstocks and production process on malonic acid, succinic acid, fumaric acid, adipic acid, azelaic acid, maleic anhydride, succinic anhydride, glutaric anhydride. These diacids or diacid anhydrides can be produced via natural plants and processed i.e. by fermentation or commercially available. For diols we did researches on 2,3 butanediol or 1,3-propanediol which can be produced from natural feedstocks also. For cross-linking monomers we have done some researches on acrylic acid and styrene. Acrylic acid can be produced via natural plants such as sugar by fermentation; styrene is existing in many plants also.

### Production reaction and network of polyester

Condensation reaction using diacids and glycerol, a whole variety of different kinds of polyester structure with a limited number of building parts: Varying doses of diacids versus glycerol give different kinds of polymer structure (linear, branched, high density or low density, with saturated diacid we can get linear polyester, with unsaturated diacid we can get branched polyester, with long chain diacid we can get high density polyester, while with short chain diacid we can get low density polyester. Using diacid anhydrides less water is expelled during condensation reaction, if this might give problems when curing a thermoset product in the mould.

### Conclusion

With a limited amount of different kinds of building blocks, a whole variety of different kinds of polyesters with its material properties can be made. The feedstock for diacid, diols and glycerol synthesis are commercially available, which showing that by being inspired by different compounds found in nature and using the ideas behind various polymerisation reaction making natural based polyester is technical feasible and probably commercially possible feasible in future.

## P6

# Cross-Metathesis of Unsaturated Fatty Acid Esters

Anastasiya Rybak, Michael A. R. Meier*

*University of Applied Sciences Oldenburg/Ostfriesland/Wilhelmshaven*
*Junior research group renewable raw materials, Faculty of Technology,*
*Constantiaplatz 4, 26723 Emden, Germany*
**E-mail: michael.meier@fh-oow.de; Internet: http://www.meier-michael.com*

In view of the continuous decrease of fossil resources and increasing ecological damages, the aspects of a sustainable use of renewable raw materials have to be more and more taken into consideration.[1,2] Especially for the conversion of these resources into innovative new materials as well as already existing chemical intermediates new and improved chemical approaches are required.

Olefin metathesis has emerged as a powerful tool for synthetic organic as well as polymer chemistry.[3] As all other metathesis reactions, olefin metathesis is a process involving the exchange of a bond (or bonds) between similar interacting chemical species so that the bonding affiliations in the products are identical (or closely similar) to those in the reactants.[4] Practically, this results in the exchange of substituents of two reacting double bonds, a transalkylidenation. In particular, the metathesis of fatty acid derivatives, obtained from plant oils, is a promising catalytic route that can be used for the synthesis of chemical intermediates from renewable raw materials.[5,6]

Our research applies the ruthenium-catalyzed cross metathesis reaction of unsaturated fatty acid esters (e.g. methyl oleate, methyl erucate or methyl 10-undecenoate) with various substituted olefins (e.g. 2-butene-1,4-diol, styrene, or methyl acrylate). The resulting functionalized esters are promising monomers for the synthesis of (novel) polymeric materials from renewable resources. Within this contribution, we will focus our discussion on the synthesis of the mentioned monomers describing in detail the use of different metathesis catalysts and reactions conditions.

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P7

# Polymers from renewable resources: 2-oxazolines from plant oils

Patrice A. Fokou, Michael A. R. Meier*

*University of Applied Sciences Oldenburg/Ostfriesland/Wilhelmshaven*
*Junior research group renewable raw materials, Faculty of Technology,*
*Constantiaplatz 4, 26723 Emden, Germany*
**E-mail: michael.meier@fh-oow.de; Internet: http://www.meier-michael.com*

The problem of global warming has evolved as an effect of atmospheric accumulation of green house gases, the most important of these gases being carbon dioxide ($CO_2$). In order to meet the future energy as well as raw material demands without increasing the emission of these green houses gases, the substitution of fossil resources with renewable raw materials is a very promising approach. It has been shown already that renewable resources are a useful basis for the synthesis of a variety of monomers for linear as well as cross-linked polymers of different types (e.g. polyolefins, polyesters, polyamides, epoxy and polyurethane resins).

Oxazolines have played an increasingly important role in many areas of chemistry.[1] They are widely used as monomers in polymer chemistry,[2] as synthetic reagents,[1,3] and most recently as ligands in asymmetric synthesis.[3] Alkyl- and aryl-substituted 2-oxazolines are also present in marine natural products and are important pharmacophores in numerous bioactive natural products[4] that display cytotoxic, antitumor, neuroprotective, antibiotic, or antifungal properties.[5] As a result of this interest in oxazolines, several methods for the synthesis of 2-oxazolines have been developed. In particular, the reaction of amino alcohols with acid chlorides, carboxylic acids, and nitriles are commonly used.[1]

Here we describe the preparation of 2-oxazolines from plant oil renewable resources with the goal to polymerize the resulting monomers in a living/controlled fashion offering possibilities to obtain defined block copolymers from renewable resources. As an example in this direction, it was recently shown in the literature that a soy-based 2-oxazoline monomer (SoyOx) could be polymerized in a controlled/living fashion under microwave irradiation.[6] Extending this example, we will focus our discussion on model monomers and polymers, describe their synthesis, polymerization as well as the properties of the resulting polymers.

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**P8**

# Acrylate and Methacrylate Monomers from plant oils

Tina Jacobs, Marco Schubert, Michael A. R. Meier*

*University of Applied Sciences Oldenburg/Ostfriesland/Wilhelmshaven*
*Junior research group renewable raw materials, Faculty of Technology,*
*Constantiaplatz 4, 26723 Emden, Germany*
**E-mail: michael.meier@fh-oow.de; Internet: http://www.meier-michael.com*

Monomers based on fatty alcohol acrylates or methacrylates are well known in industry and applied as low $T_g$ monomers in copolymers of various kinds. However, even if these monomers are well known they have only been studied to a very little extent. A Scifinder$^{TM}$ search for these monomers by registry number revealed that surprisingly little scientific literature is available for all alcohol acrylates or methacrylates. Moreover, to our surprise, very little is reported in the literature concerning living or controlled polymerisation techniques of plant oil derived monomers. The most frequently reported controlled polymerisation technique applying fatty acid derived monomers seems to be atom transfer radical polymerization (ATRP), whereas other controlled radical polymerisation techniques, such as nitroxide mediated polymerisation (NMP) or reversible addition–fragmentation chain transfer (RAFT) polymerisation, were to the best of our knowledge not yet applied to such monomers. For instance, a variety of ligands was studied for the polymerisation of lauryl methacrylate (LMA) by ATRP revealing that bipyridyl based ligands could not adequately control the polymerisation.[1] Moreover, controlled polymerisation of higher alkyl methacrylates, e.g. LMA and stearyl methacrylate (SMA), has been successfully achieved by bulk ATRP at ambient temperature using CuCl/PMDETA/tricaprylylmethylammonium chloride (Aliquatw336) as the catalyst system and ethyl 2-bromoisobutyrate as the initiator.[2] However, improved control was achieved if THF was added to the system. Furthermore, the ATRP of LMA in different solvents with ethyl 2-bromobutyrate as initiator and CuCl/PMDETA as the catalysts has been investigated.[3] The rate of polymerisation followed first order kinetics with respect to the monomer and was faster in *N,N*-dimethylformamide than that in other solvents (acetonitrile, anisole, benzene, or toluene).
Since these first reports provide only a limited amount of knowledge, a detailed study of the polymerisation kinetics and (co)-polymerisation behaviour of these monomers, especially with controlled polymerization techniques, as well as the properties of the resulting polymers is a prerequisite to close this knowledge gap and to open new avenues for these natural resource derived materials with potential applications. However, as a first step of these investigations we will discuss the synthesis and characterization of the described long alkyl chain Acrylates- and Methacrylates as well as novel branched Methacrylate derivatives that are derived from fatty alcohols.

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# List of Participants

**Dr. Hanan Atia**
Leibniz-Institut für Katalyse e. V. an der
Universität Rostock, Außenstelle Berlin
Richard-Willstätter-Straße 12
12489 Berlin, Germany
+49 (0)30-63924153
hanan.atia@catalysis.de

**Prof. Dr. Joël Barrault**
Université de Poitiers
40, av. du recteur Pineau
86022 Poitiers cedex, France
+33 (0) 5 49 45 39 99
joel.barrault@univ-poitiers.fr

**Dr. Franz-Erich Baumann**
Degussa GmbH
Paul-Baumann-Str. 1
45764 Marl, Germany
+49 (0)2365495967
franz-erich.baumann@degussa.com

**Prof. Dr. Matthias Beller**
Leibniz-Institut für Organische Katalyse
an der Universität Rostock e.V.
A.-Einstein-Str. 29a
18059 Rostock, Germany
+49 (0)381 1281-113
Matthias.Beller@catalysis.de

**Dr. Toine Biemans**
Worlée-Chemie G.m.b.H.
Söllerstr. 16
21481 Lauenburg, Germany
+49 (0)4153 596 4760
TBiemans@ch.worlee.de

**Dr. Ursula Biermann**
Carl von Ossietzky Universität Oldenburg
Postfach 2503
26111 Oldenburg, Germany
+49 (0)441 7983725
ursula.biermann@uni-oldenburg.de

**Dr. Paul Birnbrich**
Cognis
FP - Development (R&D)
40551 Düsseldorf, Germany
+49 (0)211-7940-2279
paul.birnbrich@cognis.com

**Dr. Roderick Bouvy**
NPSP
Küppersweg 31
2031 EA Haarlem, The Netherlands
+31 (0)23-55-12328
roderick.bouvy@npsp.nl

**Gökhan Çayli**
Boğaziçi University
Kimya Bolumu. Kare Blok.
Kuzey kampus. Bebek
P.Kod: 34342
Istanbul, Turkey
cayli@boun.edu.tr

**Dr.-Ing. Joosten Connemann**
Ölmühle Connemann GmbH
Sägemühlenstr. 49
26789 Leer, Germany
+49 (0)491-9276513
jc@conne.net

**Dr. Manfred Diedering**
ALBERDINGK BOLEY GmbH
Düsseldorfer Str. 39
47829 Krefeld, Germany
+49 (0) 2151 528-136
M.Diedering@alberdingk-boley.de

**Thomas Eichler**
Arizona Chemical
Christinerstr. 7
46537 Dinslaken, Germany
+49 (0)2064 479635
thomas.eichler@azachem.com

**Willi Feder**
BioPin
Linumweg 1-8
26441 Jever, Germany
+49 (0)4461-757586
willi.feder@biopin.de

**Dr. Patrice Fokou**
Fachhochschule OOW
Constantiaplatz 4
26723 Emden, Germany
+49 (0)4921 8071561
patrice.fokou@fh-oow.de

**Dr. Oliver Franke**
Clariant Produkte (Deutschland) GmbH
Werk Gendorf
84504 Burgkirchen, Germany
+49 (0)8679 7 5278
oliver.franke@clariant.com

**Erik Friedrich**
Fachhochschule OOW
Constantiaplatz 4
26723 Emden, Germany
erik_friedrich@yahoo.de

**Dr. Harold Gankema**
Arizona Chemical
Transistorstraat 16
1322 CE Almere, The Netherland
+31 (0)36 5462930
harold.gankema@azchem.com

**Prof. Dr. John George**
The City College of New York,
Department of Chemistry
Convent Avenue at 138th Street
NY 10031, New York, USA
+1 212 650 8353
john@sci.ccny.cuny.edu

**Dr. Michael Graß**
Oxeno Olefinchemie GmbH
Paul-Baumann-Str. 1
45772 Marl, Germany
+49 (0)2365-499882
michael.grass@degussa.com

**Dr. Matteo Guidotti**
Istituto di Scienze e Tecnologie
Molecolari Chimica Inorganica e
Metallorganica
Via G. Venezian, 21
20133 Milano, Italy
+39 (0)2 50314428
m.guidotti@istm.cnr.it

**Dr. Harald Häger**
Degussa GmbH
45764 Marl, Germany
+49 (0)2365492351
Harald.Haeger@degussa.com

**Mutlu Hatice**
Boğaziçi University
Boğaziçi University
Kimya Bolumu. Kare Blok.
Kuzey kampus. Bebek
P.Kod: 34342
Istanbul, Turkey
hatice.mutlu@boun.edu.tr

**Dr. Peter Höhlein**
LUTIMA
Wildbahn 4
26160 Bad Zwischenahn, Germany
+49 (0)4486 8785
P.Hoehlein@t-online.de

**Dr. Norbert Holst**
Fachagentur Nachwachsende Rohstoffe
Hofplatz 1
18276 Gülzow, Germany
+49 (0)384-6930-118
n.holst@fnr.de

**Tina Jacobs**
Fachhochschule OOW
Constantiaplatz 4
26723 Emden, Germany
+49 (0)4921 8071533
tina.jacobs@fho-emden.de

**Çavuşoğlu Jesmi**
Boğaziçi University
Boğaziçi University
Kimya Bolumu. Kare Blok.
Kuzey kampus. Bebek
P.Kod: 34342
Istanbul, Turkey
jesmi.cavusoglu@boun.edu.tr

**Xin Jin**
Delft University of Technology
Delft, The Netherlands
+31 (0)650425617
X.Jin-1@student.tudelfe.nl

**Prof. Dr. Walter Kaminsky**
Universität Hamburg
Bundesstr. 45
20146 Hamburg, Germany
+49 (0)40 42838-3162
kaminsky@chemie.uni-hamburg.de

**Prof. Dr. Cor Koning**
Eindhoven University of Technology
PO Box 513, Helix STO 1.35
5600 MB Eindhoven, The Netherlands
+31 (0)40 247 5353
c.e.koning@tue.nl

**Prof. Dr. Udo Kragl**
Universität Rostock
Siebensternweg 17
18198 Kritzmow, Germany
+49 (0)381 498 6450
udo.kragl@uni-rostock.de

**Dr. Yuni Krisnandi**
Leibniz-Institut für Katalyse e. V. an der
Universität Rostock, Außenstelle Berlin
Richard-Willstätter-Straße 12
12489 Berlin, Germany
+49 (0)30-63924153
yuni.krisnandi@catalysis.de

**Dr. Gerhard Langstein**
Bayer Material Science AG
Geb. B211
51368 Leverkusen, Germany
+49 (0)214-3057695
gerhard.langstein@bayerbms.com

**Julia Leschinski**
Universität Dortmund
Emil-Figge-Str. 66
44227 Dortmund, Germany
+49 (0)231-755-4335
Julia.Leschinski@bci.uni-dortmund.de

**Dr. Jan Lifka**
Universität Jena
Lessingstr. 12
07743 Jena, Germany
+49 (0)3641-948414
jan-lifka@web.de

**Dr. Andreas Martin**
Leibniz-Institut für Katalyse e. V. an der
Universität Rostock, Außenstelle Berlin
Richard-Willstätter-Straße 12
12489 Berlin, Germany
+49 (0)30-6392 4306
andreas.martin@catalysis.de

**Dr. Michael Meier**
Fachhochschule OOW
Constantiaplatz 4
26723 Emden, Germany
+49 (0)4921 8071587
michael.meier@fh-oow.de

**Prof. Dr. Jürgen Metzger**
Carl von Ossietzky Universität Oldenburg
Postfach 2503
26111 Oldenburg, Germany
+49 (0)441 7983718
juergen.metzger@uni-oldenburg.de

**Dr. Fabrizio Miccichè**
Delft University of Technology
Kluyverweg 1
2629 HS Delft, The Netherlands
+31 (0)15 2781607
f.micciche@tudelft.nl

**Dr. Roman Procházka**
BASF AG
Carl-Bosch-Str.
67056 Ludwigshafen, Germany
+49 (0)621 6055712
roman.prohazka@basf.com

**Dr. Herbert Riepl**
Technische Universität München,
Wissenschaftszentrum Straubing
Petersgasse 18
94315 Straubing, Germany
+49 (0)9421 187120
herbert.riepl@wzw.tum.de

**Prof. Dr. Mark Rüsch gen. Klaas**
Hochschule Neubrandenburg
Brodaer Str. 2
17033 Neubrandenburg, Germany
+49 (0)395-5693518
ruesch.gen.klaas@hs-nb.de

**Dr. Anastasiya Rybak**
Fachhochschule OOW
Constantiaplatz 4
26723 Emden, Germany
+49 (0)4921 8071510
anastasiya.rybak@fh-oow.de

**Dr. Markus Scherer**
Cognis Oleochemicals GmbH
Henkelstr. 67
40551 Düsseldorf, Germany
+49 (0)211-79404088
markus.scherer@cognis.com

**Prof. Andrzej Sobkowiak**
Rzeszow University of Technology
P.O. Box 85
35-959 Rzeszow, Poland
+48 (0)603-950-688
asobkow@prz.edu.pl

**Dr. Achim Stankowiak**
Clariant Produkte (Deutschland) GmbH
Werk Gendorf
84504 Burgkirchen, Germany
+49 (0)8679 7 5278
achim.stankowiak@clariant.com

**Prof. Dr. Christian Stevens**
Faculty of Bioscience Engineering
Gent University
Coupure Links 653
9000 Gent, Belgium
+32 (0)9 264 58 60
Chris.Stevens@UGent.be

**Dr. Marian Steverink**
Uniqema Nederland B.V.
Buurtje 1
2802 BE, Gouda, The Netherlands
+31 (0)182-542809
marian.steverink@uniqema.com

**Paeglis Talis**
Riga Technical University
Kalku 1
Riga, Latvia
+37 (0)1 26361622
Tali_ban@inbox.lv

**Dr. Peter Tollington**
Uniqema Nederland B.V.
Buurtje 1
2802 BE, Gouda
The Netherlands
+31 (0)182542254
peter.tollington@uniqema.com

**Dr. Elisabetta Usai**
University of Cagliari
Cittadelle Universitaria S.S. 554 Bivio per Sestu
Monserrato, Italy
+39 (0)70 6754423
elisabetta.usai@tele2.it

**Ilona Vanaga**
Riga Technical University
Kalku 1
Riga, Latvia
+37 (0)1 29554716
Vilony@gmail.com

**Dr. Tomas Vlček**
Synpro Inc.
S.K. Neumanna 1316
Pardubice, Czech Republic
+42 0466067207
tomas.vlcek@synpro.cz

**Michael Volland**
Degussa GmbH
Paul-Baumann-Str. 1
45764 Marl, Germany
+49 (0)2365-495247
michael.volland@degussa.com

**Prof. Dr. Klaus-Dieter Vorlop**
Bundesforschungsanstalt für
Landwirtschaft
Bundesallee 50
38116 Braunschweig, Germany
+49 (0)531 596 4101
klaus.vorlop@fal.de

**J. Vreeswyk**
Uniqema Nederland B.V.
Buurtje 1
2802 BE Gouda, The Netherland
+31 (0)182-542280
hans.vreeswijk@uniqema.com

**Weber Weber**
Saria Bioindustries
Wernerstr. 95
59379 Selm, Germany
+49 (0)2592-210145
michael.weber@ecomotion-gmbh.de

**Dr. Alfred Westfechtel**
Cognis Oleochemicals GmbH
Henkelstr. 67
40589 Düsseldorf, Germany
+49 (0)221-79402793
alfred.westfechtel@cognis-
oleochemicals.com

**Dr. Veronika Wloka**
BASF AG
Carl-Bosch-Str. 38
67056 Ludwigshafen, Germany
+49 (0)621-6078494
veronika.wloka@basf.com

**Dr. Christian Zimmer**
Universität Greifswald
Felix-Hausdorff-Str. 4
17487 Greifswald, Germany
+49 (0)38348622813
christian.zimmer@uni-greifswald.de