Macromol. Symp. **2010**, 293, 39–42 DOI: 10.1002/masy.200900041

Self Metathesis of Fatty Alcohols and Amines to Provide Monomers for Polyester and Polyamide Products

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Summary: Self metathesis of oleochemicals offers a variety of bifunctional compounds, that can be used as monomer for polymer production. Many precursors are in huge scales available, like oleic acid ester (biodiesel), oleyl alcohol (tensides), oleyl amines (tensides, lubricants). We show several ways to produce and separate and purify C_{18}-α,ω-bifunctional compounds, using Grubbs 2nd Generation catalysts, starting from technical grade educts.

Keywords: fatty acid; metathesis; polyamide; polyester; renewable resources

Introduction

Among the applications of natural products in the chemical industry, one of the oldest fields beside cellulose is the use of plant derived fats and oils, the trigylcerides. The tenside industry traditionally consumes the largest part of the world wide primary production apart from food & feed for synthesis of fatty acid ethoxylates, fat alcohols, fat sulfonates, fat amines and many derivatives thereof. [1]

The polymer industry has been another field of applications e.g. some very old inventions based on the cross-linking of epoxidized fatty acids, e.g. resins from soy oil, or the german trademark ‘‘linoleum’’. Modern specialty polyesters or polyamides in a more expensive market segment would be a possible additional field of applications.

Thermoplastic elastomers are block-copolymers of different oligoesters and amides distinguished by grossly different glass transition temperatures providing definite amorphous and crystalline sections. In this field not only α,ω-functionalized monomers of short and medium chain length will be needed, but also C_{14} to C_{18} will find application in manufacturing amorphous polymer blocks.

One of the shortcomings of olefinic natural fatty acids is the situation of the double bond at C9/C10 or around that. To date, only ozonolysis of oleic acid and thermal treatment of ricinoic acid yield industrially relevant monomer feed stocks [2,3], e.g. azelainic acid and undecenoic acid having a shorter chain length. The field of longer carbon chains can be accessed via chemistry of the double bond. Transition metal catalyzed metathesis of the double bond with ethylene is an innovative means of cleaving the readily available oleic acid to yield decenoic acid, also making no use of the C_{18} hydrocarbon oleic acid effectively is. In the absence of other olefins as a partner, oleic acid is subject to self metathesis, yielding octadec-9-endioic acid and octadec-9-ene. [4–6] Despite the loss of the carbon chain beyond C_9, this reaction is therefore an entry to the field of

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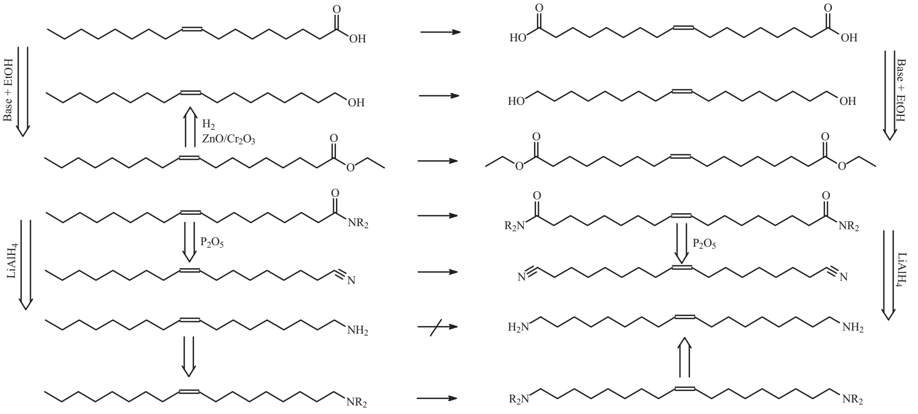


Figure 1.
Metathetic conversions of oleochemicals and chemical modifications to produce a variety of possible monomers.

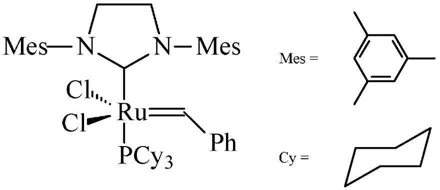
ω-functionalisation of oleic acid, which is generally difficult.

The tolerance of water and functional groups by many of the recently developed Grubbs- Ru – catalysts may open doors to industrial applicability of substrates impossible to deal with under catalysis by older Re, W or Mo metathesis systems. This system seems hardly applicable in industry due to the need of extensive purification of the substrates. Nevertheless it is reactive and was examined as early as 1972.[7,8] Feed streams in petrochemistry usually consist of low-boiling, short-chained hydrocarbons, which easily can be distilled or striped off. Distilling oleochemicals from natural products usually affords ultra high vacuum manipulation under special conditions. With respect to the economic needs of a technical application of oleochemicals in the field of polyesters or polyurethanes, Ru-based systems seem to be more promising due to the reduced need of purification of substrates.

Industrial oleochemistry – the tenside industry – provides a variety of coumpounds on large scale, which are a potential substrate for metathetic manufacture of ω-functionalised fatty acid derivatives. Besides the different oleic esters there are oleyl alcohol and fatty amines. It is the scope of this work to provide large scale reaction data and chemical properties of resultant molecules relevant as monomers.

Results

Due to its intensive use as fuel, the most abundant oleic esters are oleic acid methyl and ethyl esters, mainly from brasil. In a solvent free reaction regime – the only means compatible with a later ultra high vacuum distillation because of deteriorating effect of traces of solvents to the vacuum manipulators – a maximum of about 25% content was achieved with a substrate / catalyst ratio (Grubbs 2nd Generation, see Figure 2) as low as 1/120000. The low ratio was only achieved with highly purified oleic acid esters, when using technical grade educts (Aldrich 317675), the ratio was ten times higher (0.1 mol-%). This concentration hardly could be improved by addition of certain compounds according to an example.[9] Batches with up to 2 kg oleic acid ester could to be converted. A stepwise separation of the main products present in



C1

Figure 2.
utilized catalyst for self metathesis of oleochemicals.

the reaction solution is possible via thin film distillation. By adjusting the applied pressure, first octadecene, then oleic acid ester and at last octadec-9-endioic acid ester can be obtained in high purities.

Subjecting the resultant pure oleic ester to repeated metathesis, a total distilled yield of nearly 48% was achieved. The yields with oleic acid methyl ester were far inferior to the ethyl ester. This is due to the fact that the boiling points of oleic acid methyl ester and octadec-9-en-1,18-dicarboxylic acid dimethyl ester being closer than the ethyl ester and therefore are more difficult to separate via distillation. Oleic Acid itself was subjected to successfully metathesis recently.[10]

Protected oleyl alcohols are known to produce α,ω-diols.[11,12] Acetylated oleyl alcohol subjected to metathesis gives nearly the same yield as oleic acid esters. This is not surprising, since the olefinic double bond in oleic acid ethyl ester and acetic acid oleyl ester are nearly identical in structure and physico-chemical properties. A separation of the protected diol via thin film evaporation is possible. Oleyl alcohol (technical grade, Aldrich 369314) itself, subjected to C1, produces octadec-9-en-1,18-diol, but in a lower yield (20%) with a catalyst loading of 0.1 mol-%. This is due to catalyst decomposition reactions with primary alcohols [13] and impurities in the product. Surprisingly, the diol precipitates after cooling of the reaction solution. The pure product was obtained after filtration through a 16 mesh sieve and recrystallization at a scale of up to 1 kg batches. Lowering the reaction temperature from 55 °C to 25 °C did not result in a higher yield. After one hour the reaction is nearly completed (See Figure 3). Metathesis at room temperature is possible, with analog yields and catalyst loadings.

Oleic acid amide is an oleochemical intermediate necessary for the production of oleylnitrile and oleyl amine [14]. N-mono, di-alkylated Amides as well as the oleic acid amid were subjected to self metathesis. Oleic acid N,N-diethylamide can be transformed with yields comparable to oleic acid esters (20-25%). The yields of the mono-ethyl (10%) and free amide (5%) are lower, which may be due to the basicity of the heteroatom and the considerable low tolerance of C1 catalyst towards basic nitrogen. But the obtained 1,18-diamides (Octadec-9-en-1,18-dicarboxylic acid N,N′-ethylamide and Otcadec-9-en-1,18-dicarboxylic acid amide) precipitate during reaction and are easily separated from the reaction solution, the pure bifunctional compounds are obtained by centrifugation and recrystallisation. The two obtainable bifunctional

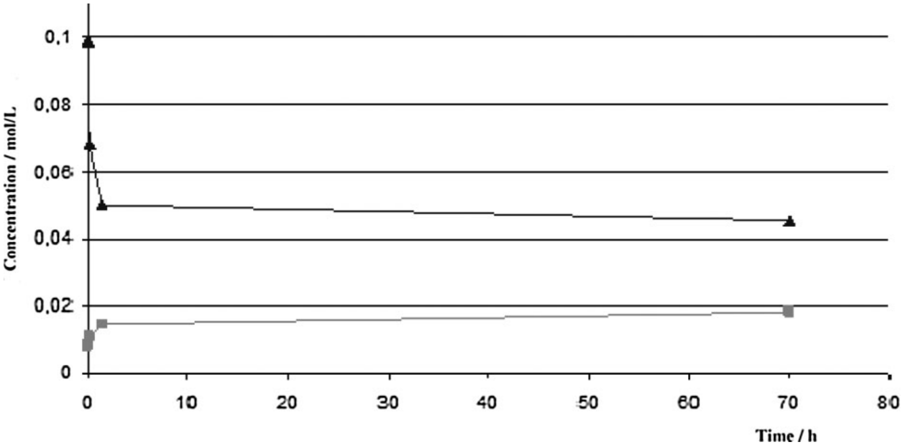


Figure 3.

Concentration gradient of Octadecenol (triangle) and Octadecen-1,18-diol (square) during self metathesis, determined via GC-MS.

Table 1.
Yields and Separation methods of selected oleochemicals

Oleochemical	Catalyst usage	Yield	Separation method
Oleic acid esters	C1, 0.01-0.1 mol%	25% Dioic ester	Thin film evaporation*
Acetic acid oleyl ester	C1, 0.1 mol%	25% actylated diol	Thin film evaporation*
Oleyl alcohol	C1, 0.1 mol%	20%	Crystallization
Oleic acid N,N-diethyl amide	C1, 0.1 mol%	25%	Thin Film evaporation*
Oleic acid N-ethyl amide	C1, 0.1 mol%	10%	Precipitation, Centrifugation
Oleic acid amide	C1, 0.1 mol%	5%	Precipitation, Centrifugation

*using VTA thin film evaporation apparatus VKL 70, 4 dm^2 evaporation surface; Octadec-9-ene is obtained at 100 °C at 0.033 mbar; Oleic acid ethyl ester is obtained at 120 °C at 0.0008 mbar; Octadec-9-ene-1,18-dioic acid diethyl ester is obtained at 130 °C at 0.0008 mbar, yielding a small residing fraction, containing nearly all ruthenium.

compounds, the C_{18}-dicarboxylic acid amide and the C_{18}-diamine are possible monomers for polyesters and polyamides.

Unfortunately oleyl amine itself undergoes almost no self metathesis. The high basicity seems to inhibit the catalyst. Acetic acid oleyl ester shows a similar yield as oleic acid monoethyl amide (5-10%) and also precipitate during reaction. Pure products were obtained via centrifugation and recrystallisation.

Conclusion

Selfmetathesis of commercially oleochemicals offers a variety of bifunctional compounds, that can be used as monomer for polymer production, if product separation is sufficiently addressed. Many precursors are available in huge scales, like oleyl alcohol (tensides), oleyl amines (tensides, lubricants). The catalyst system is able to work with technical products, although the catalyst usage will be significantly elevated then (0.01 mol-% for pure compounds, 0.1 mol-% for technical grade compounds). The separation can be done via distillation at low pressures. An exciting alternative is seen in exploiting the crystallization properties of the bifunctional compounds. Precipitating either directly during reaction or after cooling of the reaction, will be a promising technique, because it is energy saving and cheap.

Acknowledgements: This project was funded by the Fachagentur Nachwachsende Rohstoffe (FNR) Special acknowledgement is given to VTA Verfahrenstechnische Anlagen GmbH Deggendorf, especially Dipl. Ing. T. Lehmann for technical support.

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