Zuerst ersch. in : *Biobased monomers, polymers, and materials / Patrick Smith ; Richard Gross [u.a.]. - Washington, DC : American Chemical Society, 2012. - S. 151-164. - ISBN13: 9780841227675*

Long-Chain Polyesters via Chemical Catalytic Conversions of Fatty Acid Esters

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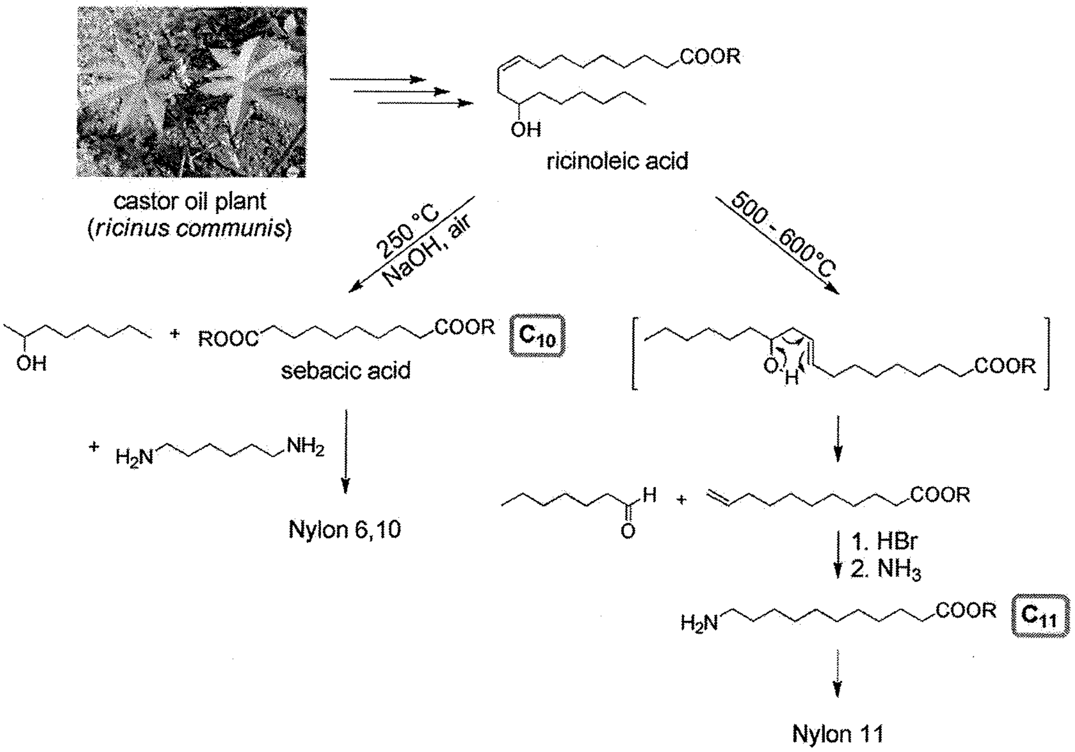
Plant oils with their long linear methylene sequences are attractive substrates for polymeric materials, such as long-chain aliphatic polyesters and polyamides. Existing biotechnological routes for their conversion to long-chain linear α,ω-dicarboxylic acid derivatives have recently been complemented by chemical catalytic conversions. This contribution discusses and compares the conversion of unsaturated fatty acids by olefin metathesis and by isomerizing alkoxycarbonylation, and reviews properties of resulting long-chain aliphatic polyesters. The impact of multiple unsaturated fatty acids present in technical grade plant oils is adressed.

Introduction

At present the chemical industry predominantly relies on fossil feedstocks. This in particular applies to polymer production which is one of the major consumers of these raw materials within the chemical industry. While the predominance of fossil feedstocks will prevail for the forseeable future, the demand for utilization of renewable feedstocks (*1–3*) is increasing due to various issues. On the very long term, the range of fossil feedstocks is limited. Shorter term arguments are the problematic volatility of crude oil prices, the security of supply and the mitigation of greenhouse gases.

At the same time, renewable feedstocks can provide access to polymeric materials with microstructures difficult to generate from fossil feedstocks, and corresponding desirable properties. Fatty acids from plant oils are attractive substrates in this respect (*4–6*) as they contain long-chain linear hydrocarbon segments as well as a carboxy group which is suited for polycondensation or conversion to other functional groups. The hydrocarbon segments can provide e.g. crystallinity, a reduced water uptake and dimensional stability, or flexible segments in polycondensates.

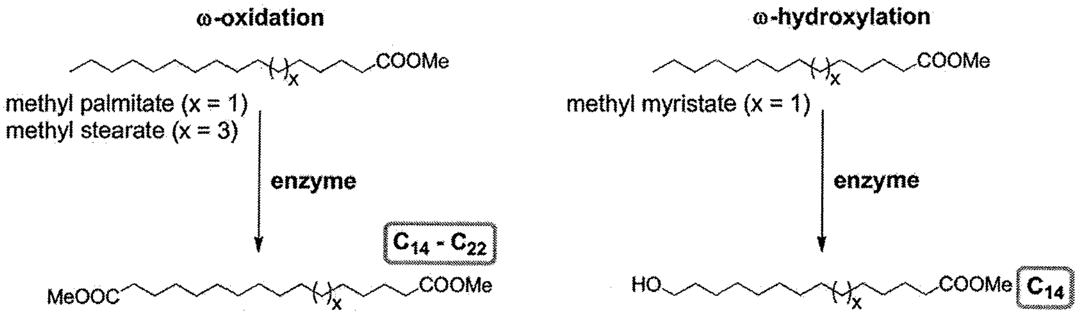


Scheme 1. Medium chain length monomers and polyamides from ricinoleic acid

Medium chain length (number of carbon atoms ranging from 6 to 13) polycondensation monomers have been prepared from ricinoleic acid esters, the major component of castor oil, since many years. Nylon-11 is generated via thermal rearrangement with chain cleavage to yield undecenoic acid (*7*). Likewise, sebacic acid, which is polymerized to Nylon-6,10, is generated by base-catalyzed cleavage of ricinoleic acid (Scheme 1) (*8*). Both of these routes require a hydroxy substituted unsaturated fatty acid, of which ricinoleic acid is the only practically available example. Castor oil is produced on a large scale, but significantly more costly (ca. double the price) than other plant oils like soybean, palm or rapeseed oil.

Moreover, in these transformations only one side of the fatty acid chain with respect to the double bond is incorporated into the monomer and ultimately the polymer. Stoichiometric amounts of less valuable byproducts are formed. These arguments also apply to ozonolysis, which converts monounsaturated fatty acids to α,ω-diacids. The medium chain length diacids azelaic acid (C_9) and brassylic acid (C_{13}) are produced industrially by oxidative cleavage of oleic acid and erucic acid, respectively, affording pelargonic acid as a byproduct (*9*).

In order to employ the potential of the long-chain linear feedstock to provide crystallizable segments and to utilize the feedstock most efficiently, a full linear incorporation of the entire fatty acid chain is desirable. For polyesters in particular, aliphatic materials based on the aforementioned medium chain-length diacids possess low melting points problematic for thermoplastic processing (*10–14*).



Scheme 2. Biotechnological routes to α,ω-difunctional linear monomers based on different fatty acids

One possible approach to such long-chain α,ω-difunctional compounds is enzymatic ω-oxidation of fatty acids (Scheme 2.) (*15–17*). Linear aliphatic diacids with the same carbon atom number as the fatty acid starting material, that is an even number usually in the range from 14 to 22 can be obtained. Issues of interest are increased space-time yields, and catalytically active microorganisms which can be nurtured by feedstocks less costly than glucose. In a related transformation of fatty acid substrates an ω-hydroxy group is introduced at the unsubstituted hydrocarbon chain end. With modified yeast strains the C_{14} ω-hydroxy fatty acid can be obtained selectively, as reported by Gross et al recently (Scheme 2) (*18*). These unsymmetric compounds can serve as AB-type monomers for polyesters (*19*).

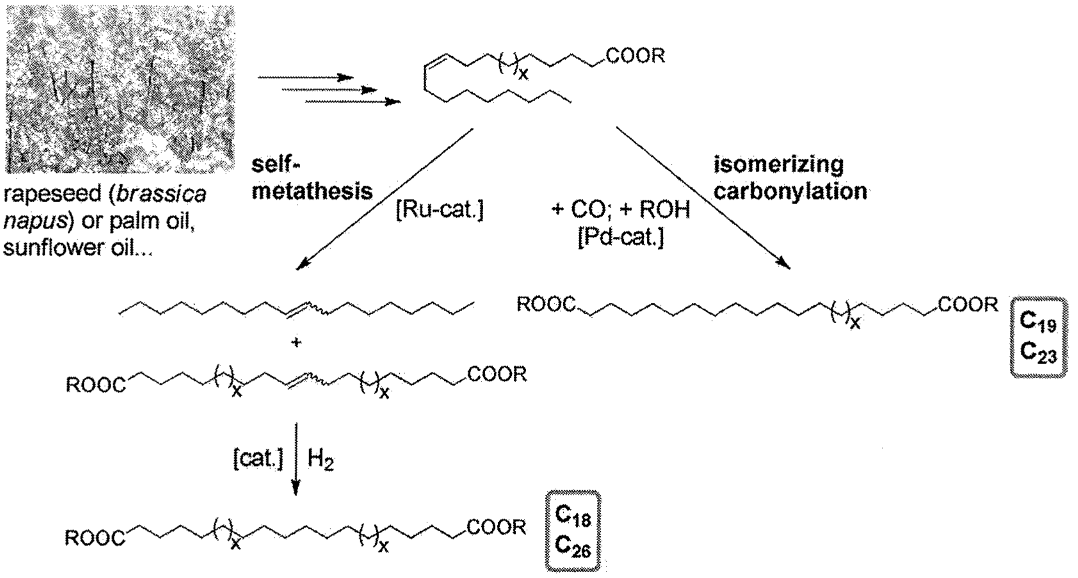
Alternatives to these biotechnological routes based on chemical catalysis have emerged more recently. Self-metathesis of unsaturated fatty acids by ruthenium alkylidenes yields even carbon number monounsaturated diacids, which can be converted to the saturated analogues by hydrogenation of the double bond. Hereby, for example 1,18-octadecanedioates are obtained from oleates. A linear internal olefin is formed as a stoichiometric byproduct (Scheme 3).

Most recently, isomerizing alkoxycarbonylation (Scheme 3) has evolved as a route to long chain α,ω-diacid esters and corresponding polycondensates (*20*). This reaction (*21*), first observed by Cole-Hamilton for fatty acid esters (*22*) converts an internal double bond deep in the hydrocarbon chain very selectively to a terminal ester group by reaction with carbon monoxide and an alcohol. Odd carbon number products are formed, e.g. 1,19-nonadecandioate from oleate.

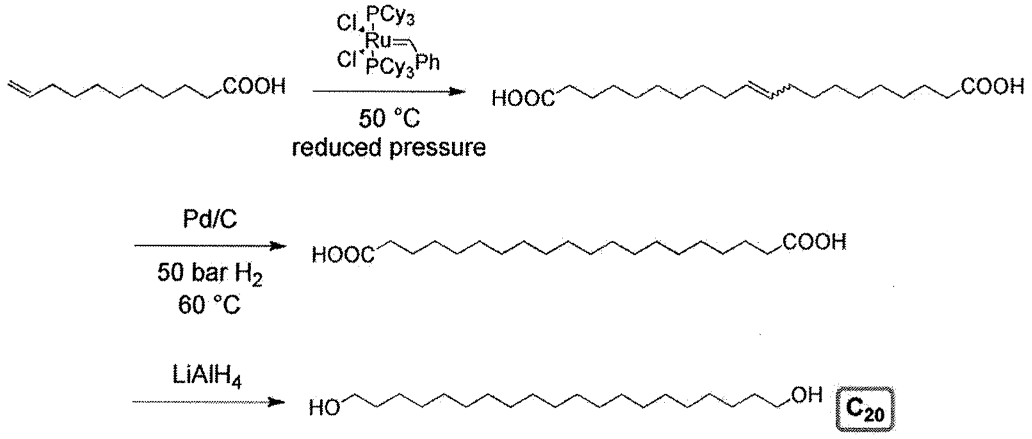
Results and Discussion

Aliphatic C_{20} Polyester from Olefin Metathesis

As an example of the generation of aliphatic long-chain polyesters via olefin metathesis routes, we have investigated C_{20} polyesters (*23*) from the self-metathesis (*24–26*) of undecenoic acid or its derivatives. Sequences of olefin metathesis, hydrogenation and reduction yield the corresponding long-chain α,ω-functionalized monomers (Scheme 4).



Scheme 3. Chemical routes to α,ω-difunctional linear monomers based on different fatty acids (x = 1: oleic acid; x = 5: erucic acid)



Scheme 4. Synthesis of C_{20} monomers for polyesterification

Pure 1,20-eicosanedioic acid (>99 %) is obtained by self-metathesis of undecenoic acid with $[(PCy_3)_2Cl_2Ru{=}CHPh]$ (Grubbs 1st generation catalyst), followed by exhaustive hydrogenation. To avoid the formation of shorter chain α,ω-difunctional products, due to metathesis of internal olefins generated from the ω-functionalized 1-olefin substrate by isomerization as a side reaction this catalyst precursor was chosen. Albeit it is known to be less reactive and less tolerant towards polar and protic functionalities by comparison to its N-heterocyclic carbene analogue $[(PCy_3)(\eta\text{-}C\text{-}C_3H_4N_2Mes_2)Cl_2Ru{=}CHPh]$ (Grubbs 2nd generation catalyst), it disfavors olefin isomerization (*27–30*). Moreover isomerization is also assumed to be reduced in the presence of carboxylic acid groups, present in the starting material (*31*, *32*).

The corresponding α,ω-functionalized diol, 1,20-eicosanediole, can be generated by reduction in high purity (also cf. Scheme 6 for catalytic hydrogenation).

Polycondensation of stoichiometric amounts of 1,20-eicosanedioc acid and eicosane-1,20-diol catalyzed by titanium alkoxides in the melt yielded poly[1,20-eicosadiyl-1,20-eicosanedioate]. The material melts with a peak temperature of T_m = 108 °C and crystallizes at T_c = 83 ° (Figure 1).

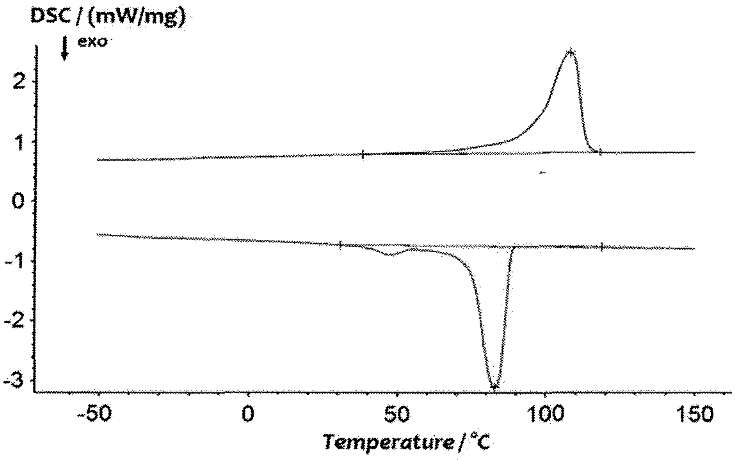
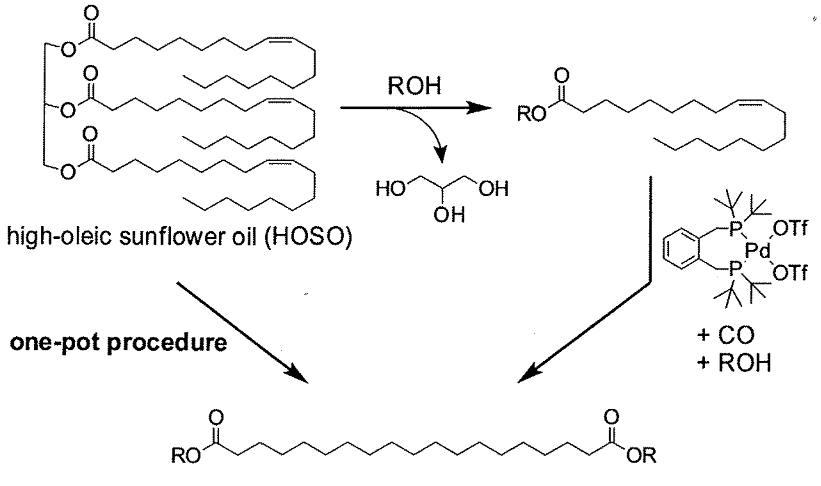


Figure 1. DSC trace of polyester-20,20 (10 K min^{-1}, 2nd heating cycle) (23).

Aliphatic C_{19} and C_{23} Polyesters from Isomerizing Alkoxycarbonylation

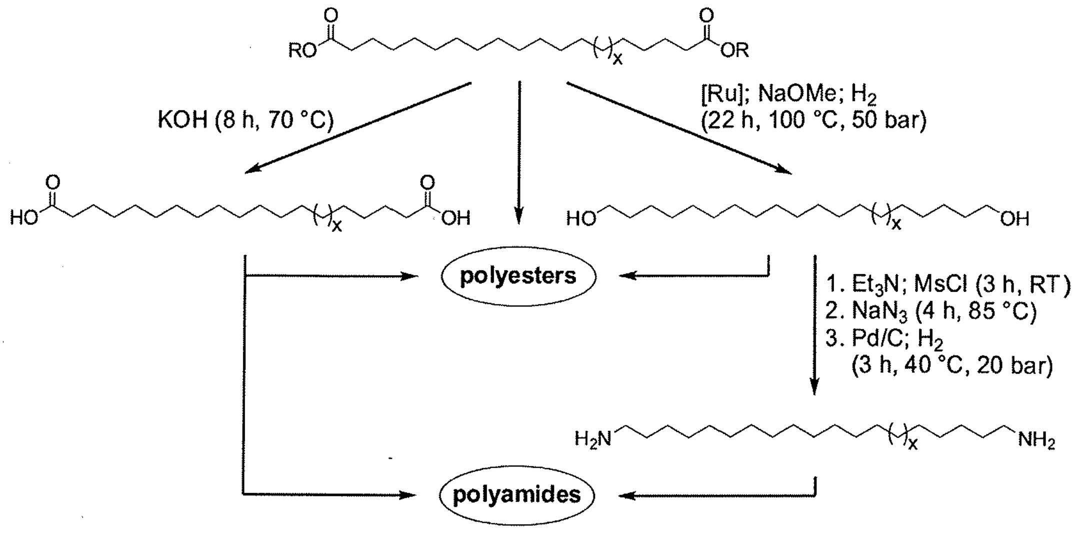
The isomerizing alkoxycarbonylation is catalyzed by palladium(II) complexes with very bulky substituted diphosphine ligands, such as 1,2-bis[(di-*tert*-butylphosphino)methyl]benzene (dtpbx). Starting from a fatty acid monoester (*20*) or, as reported recently, directly from different vegetable oils (*33*) including high oleic sunflower oil (*34*) in a one-pot procedure, α,ω-functionalized diesters can be obtained in polymerization grade purity (Scheme 5). Yields correlate with the oleate content of the starting material, but otherwise the catalyst performance appears not to vary dramatically between pure (99 %) oleate starting material and technical grade methyl oleate or triglyceride feed.



Scheme 5. Synthesis of dimethyl-1,19-nonadecanedioate starting from high-oleic sunflower oil or methyl oleate

Most plant oil sources of monounsaturated fatty acids, like oleate, contain significant amounts of the double unsaturated analogues. For example, palm oil typically contains 40 % of oleate and 10 % of linoleate in the fatty acid portion, soybean oil 25 % vs. 50 % oleate/linoleate and high oleate sun flower oil 93 % vs. 3 % (*35*). Thus, the fate of the double unsaturated fatty acids in isomerizing alkoxycarbonylation is of interest. To this end, the methoxycarbonylation of pure (≥99 %) methyl linoleate was investigated. Under typical reaction conditions, 90 °C and 20 bar CO with [κ^2-P,P-(dtbpx)Pd(OTf)] [OTf] as a well defined catalyst precursor (linoleate to Pd 125:1), the largest part of the starting material is converted as revealed by gas chromatography (GC, cf. experimental section). Of the various products formed, the main product was found to be dimethyl 1,19-nonadecenedioate. Its identity was confirmed by GC-MS, and by further reactions. Upon reacting the crude reaction mixture with bromine, the compound is not observed any more by GC. Also, catalytic hydrogenation with Pd/charcoal results in complete conversion to dimethyl 1,19-nonadecanedioate, as confirmed by enrichment with a genuine sample in GC analyses. The latter experiment also illustrates that the multiple unsaturated fatty acid can be converted to the saturated α,ω-diester by a sequence of isomerizing carbonylation and catalytic hydrogenation.

From the product of isomerizing alkoxycarbonylation of methyl oleate and ethyl erucate, respectively, dimethyl 1,19-nonadecanedioate and diethyl-1,23-tricosanedioate crystallize in >99 % purity. These novel linear long-chain substances can be utilized as platform chemicals for the synthesis of a range of α,ω-functionalized compounds, which can serve amongst others as novel polycondensation monomers (Scheme 6) (*36*). Amongst others, long-chain α,ω-diols are accessible by catalytic hydrogenation in high purity.



Scheme 6. Long-chain α,ω-difunctional compounds from unsaturated fatty acids (x = 1, oleic acid as starting material; x = 5, erucic acid) (36)

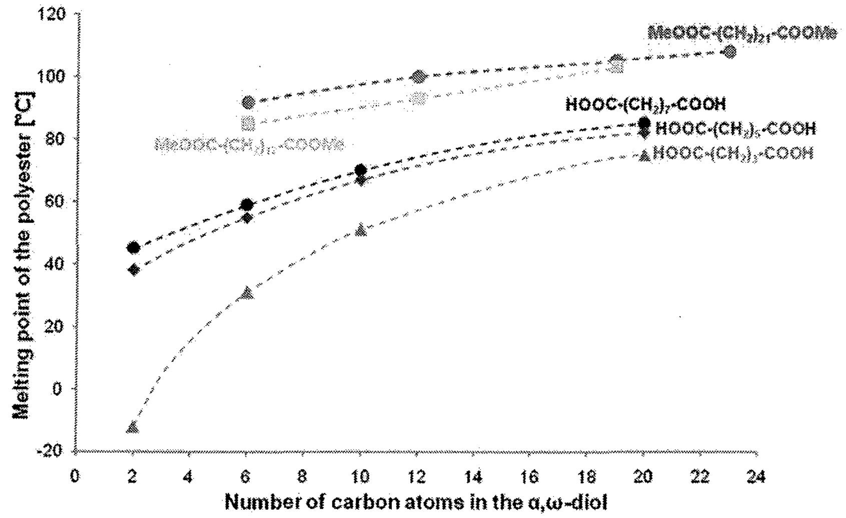


Figure 2. Melting points of polyesters obtained by polycondensation of dimethyl-1,19-nonadecanedioate and diethyl-1,23-tricosanedioate, and of azelaic, pimelic, andglutaric acid with α,ω-diols of different chain lengths (10, 20, 36).

Polyesters prepared from these long-chain dicarboxylic acid esters by polycondensation with the corresponding diols, namely poly[1,19-nonadecadiyl-1,19-nonadecanedioate] and poly[1,23-tricosadiyl-1,23-tricosanedioate], possess melting points above 100 °C and crystallization temperatures around 90 °C (*20*). These thermal properties compare with typical thermoplastics, and in this respect are significantly higher than for medium chain length aliphatic polyesters. For example, poly(decamethylene sebacate) melts at $T_m = 80$ °C (*12*). The enthalpies of fusion of the crystalline portion of these long-chain aliphatic polyesters and their crystalline structures as revealed by WAXS approach those of polyethylene, reflecting their largely hydrocarbon character. High crystallinities of $\chi = 70$ to 75 % are observed (*20*).

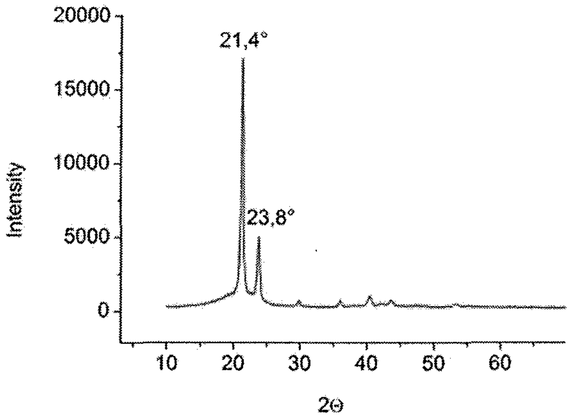
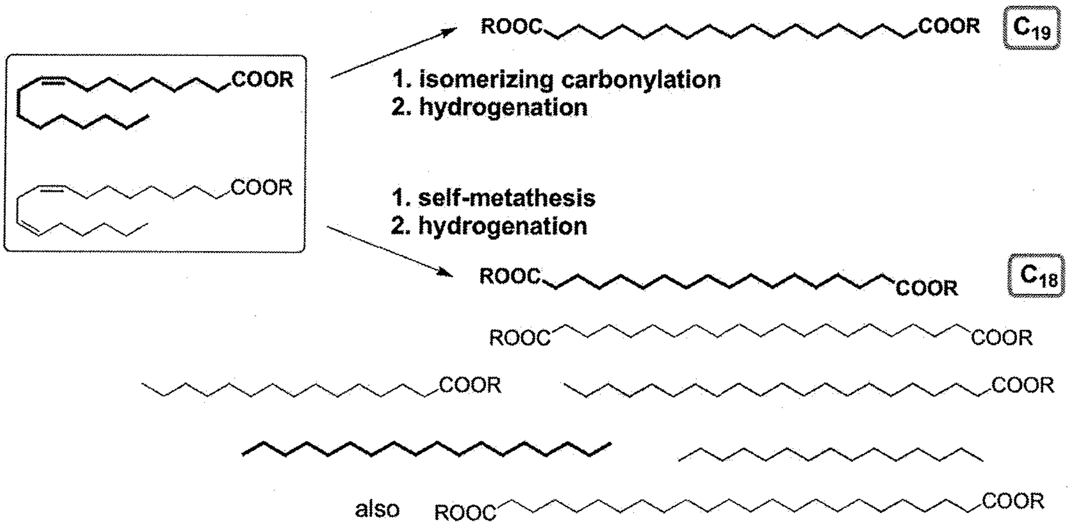


Figure 3. WAXS diffraction pattern of poly[1,6-hexadiyl-1,19-nonadecanedioate] (36).

Substantial melting and crystallization points, and crystallinities can also be achieved by combination of the long-chain diacids with shorter chain petrochemistry- or renewable-resource based monomers (Figures 2 and 3). E.g., polyesters with 1,6-hexanediole or 1,12-dodecanediole melt in the range of 86 to 100 °C, and crystallize above 70 °C.



Scheme 7. Major products obtained by isomerizing alkoxycarbonylation (top) and self-metathesis (bottom) of an oleate and its double unsaturated analogue linoleate, followed by double bond hydrogenation

Summary and Conclusion

Olefin metathesis and isomerizing alkoxycarbonylation are promising catalytic routes for the generation of long-chain α,ω-difunctional monomers, and corresponding polymers and materials. A significant difference between these two routes is the spectrum of products formed, particularly from technical plant oil feedstocks which contain substantial portions of multiple unsaturated fatty acids in addition to the monounsaturated major component. Metathesis will convert the multiple unsaturated fatty acids to additional α,ω-diacid esters of different chain length. A range of hydrocarbons is formed as stoichiometric byproducts, as illustrated in Scheme 7 for a sequence of self-metathesis and double bond hydrogenation. By contrast, in isomerizing alkoxycarbonylation the multiple unsaturated fatty acids can in principle be converted to the same α,ω-diacid esters as formed as the main product from the monounsaturated fatty acid starting material. This difference between olefin metathesis and isomerizing carbonylation can be related to a fundamental characteristic of these reactions: in olefin metathesis, often equilibria are obtained and there is no extreme kinetic preference for a particular product. The isomerizing carbonylation, on the other hand, is strictly kinetically controlled and yields a product not representing the thermodynamically favored outcome.

These considerations illustrate that metathesis of technical plant oils generates a range of interesting products for polycondensation chemistry. On the other hand, effective seperation procedures are required. Note that in a technical process, recycling of selected metathesis products prior to hydrogenation could narrow the product spectrum.

Concerning future developments, olefin metathesis of plant oils appears to be feasible on a larger scale. Concrete plans have been announced for the construction of a biorefinery for the large scale conversion of palm oil by metathesis with 1-butene. This process would yield also substantial amounts of self-metathesis byproducts, that is in particular 1,18-octadecenedioate (*37*). Isomerizing alkoxycarbonylation of plant oil has been disclosed on a kilogramm scale to date (*34*). Carbonylation reactions in general are well established processes in industry. A large scale process for the methoxycarbonylation of ethylene to methylpropionate (as a part of a novel route to MMA) which likely uses a very similar catalyst as employed here for the isomerizing alkoxycarbonylation of fatty acids went into operation in 2008 (*38*, *39*). While in the isomerizing reaction improving catalyst productivity is an issue, this illustrates the principal feasibility of such reactions.

These developments provide broad perspectives for novel polycondensates and materials. One example are thermoplastic semicrystalline aliphatic polyesters.

Experimental Section

Materials and General Considerations

Unless stated otherwise, all manipulations were carried out under inert gas atmosphere using standard Schlenk or glovebox techniques. Methanol was distilled from magnesium turnings and iodine. THF was distilled from sodium/benzophenone under inert conditions. All other solvents were used in technical grade as received. Carbon monoxide (3.7) and hydrogen (5.0) were supplied by Air Liquide. Methyl linoleate ($\geq$ 99 %) was supplied by Sigma Aldrich. All solvents were degassed by three freeze-pump-thaw cycles prior to use. Methyl palmitate ($\geq$99 %) was supplied by Sigma Aldrich and palladium/charcoal (activated; 10 % Pd) was purchased from Merck. The complex [κ^2-(P^P)Pd(OTf)][OTf] was prepared according to a previously reported method (*36*).

Gas chromatographic analysis were performed using a Perkin-Elmer (PE) Clarus 500 instrument equipped with a flame ionization detector and an Elite-5 column (crosslinked 5 % diphenyl- 95 % dimethyl polysiloxane). The temperature of the oven was kept at 90°C for 1 min, then heated from 90°C to 280°C with a heating rate of 30°C per minute and was finally held at this temperature for 8 min. Helium of 99.995 % purity was used as the carrier gas. Injector and detector temperature were both set to 280°C. A sample volume of 1 μL was injected via autosampler. Analysis of the retention times and peak areas were performed using the TotalChrom software (Perkin Elmer).

Mass spectra (GC-MS) were received from an Agilent Technologies 7890A Series GC system with an Agilent Technologies 5975C Mass Selective Detector (electron impact ionization with 70 eV). The GC apparatus was equipped with a Phenomenex ZB-5 column (5 % diphenyl- 95 % dimethylpolysiloxane) of 30 m length, 0.25 mm inner diameter and 0.25 μm film thickness. The initial temperature of 50 °C was kept for 1 min, after which the column was heated at a rate of 30 °C per minute up to 280 °C. The final temperature was kept for 8 min. Helium of 99.995 % purity was used as the carrier gas. The injection temperature was set to 250°C.

Alkoxycarbonylation of Methyl Linoleate

Carbonylations were carried out in a 20 mL stainless steel magnetically stirred pressure reactor equipped with a heating jacket and a glass inlay. Prior to a carbonylation experiment the reactor was purged several times with nitrogen. [κ^2-(P^P)Pd(OTf)] [OTf] (P^P = 1,2-bis[(di-tert-butylphosphino)methyl]benzene) (38 mg, 0.048 mmol) was weighed into a Schlenk tube under an inert atmosphere and dissolved in 10 mL of methanol. Methyl linoleate (2.0 mL; 6.0 mmol) and as an internal standard methyl palmitate (5 mol-%) were added. After stirring for a few minutes, the homogenous reaction mixture was cannula transferred into the pressure reactor. The reactor was closed, pressurized with 20 bar carbon monoxide and then heated to 90 °C. After 5 d the reactor was cooled to room temperature and vented. The crude product was dissolved in methylene chloride and filtrated over a Buchner funnel to remove solid residues. Removing the solvent in vacuo yielded a yellow oil, which was analyzed by GC (Figure 4). GC-MS analysis of the main peak (retention time 8.95 min) yielded: m/z (relative intensity) = 354 (3) [M^+]; 323 (17); 322 (24); 305 (3); 304 (6); 291 (32); 290 (54); 262 (12); 151 (11); 149 (11); 137 (16); 135 (16); 133 (12); 123 (22); 121 (22); 121 (19); 109 (28); 98 (42); 95 (53) 81 (68); 74 (62); 69 (52); 67 (64); 59 (42); 55 (100).

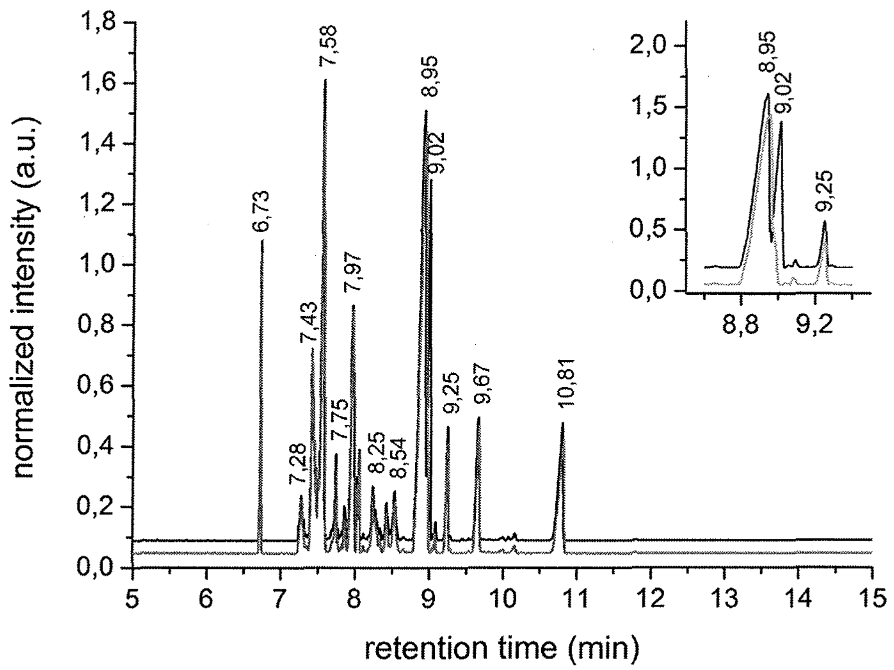


Figure 4. Gas chromatogram of the crude reaction mixture from isomerizing carbonylation of methyl linoleate. Insert: close-up of main peak (gray scale) and enrichment with a genuine sample of dimethyl 1,19-nonadecanedioate (black). Assignments of selected peaks: 6.73 min methyl palmitate added as internal standard (5.3 area %)., 7.58 methyl linoleate residual starting material (16.4 %), 8.95 dimethyl 1,19-nonadecenedioates (37.7 %), tentatively: 9.25 dimethyl 1,19-nonadec-2-endioate (3.1 %).

Catalytic Hydrogenation

The crude product of the alkoxycarbonylation of methyl linoleate was dissolved in 50 mL of dry and degassed THF. After addition of Pd/C (10 % Pd) (200 mg, 0.19 mmol Pd), the resulting mixture was cannula-transferred into a 280 mL stainless steel mechanically stirred (1500 rpm) pressure reactor equipped with a glas inlay and a heating/cooling jacket controlled by a thermocouple dipping into the reaction mixture, which was purged several times with argon prior to the reaction. The reactor was closed and pressurized with 50 bar of hydrogen and heated to 70 °C. After 12 h the reactor was cooled to room temperature and vented. The reaction mixture was then filtrated over a Buchner funnel to remove catalyst residues. After removing the solvent in vacuo an off-white solid was obtained, which was subsequently dissolved in methylene chloride and analyzed by GC (Figure 5). ^{1}H NMR shows that all double bonds are hydrogenated completely.

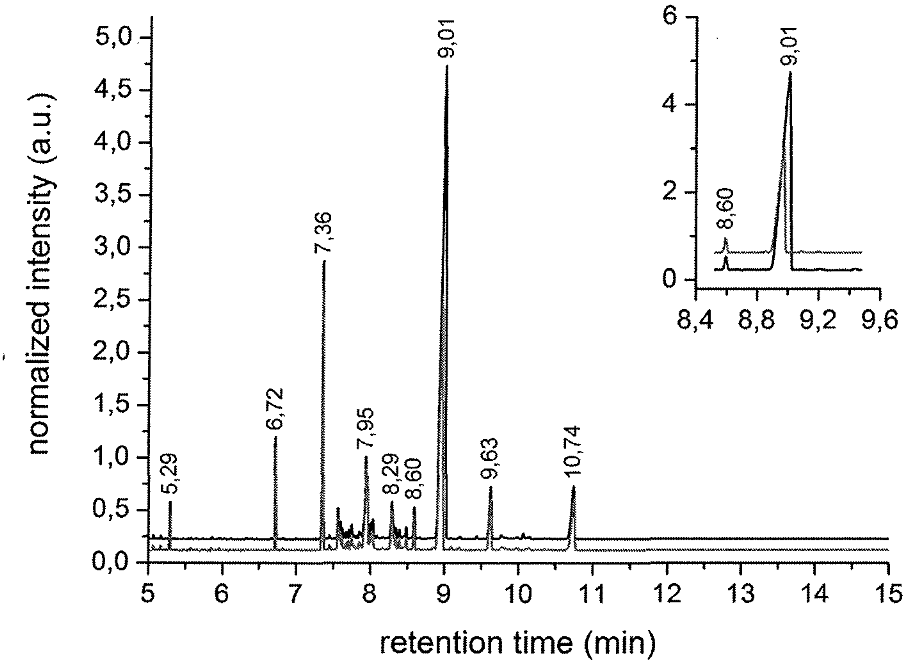


Figure 5. Gas chromatogram of hydrogenated reaction mixture from isomerizing carbonylation of methyl linoleate. Insert: close-up of main peak (gray scale) and enrichment with a genuine sample of dimethyl 1,19-nonadecanedioate (black). Assignments of selected peaks: 6.72 min methyl palmitate added as internal standard (5.2 area %), 7.36 methyl stearate (17.9 %), 9.01 dimethyl 1,19-nonadecanedioate (41.6 %).

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