Aliphatic Polyester Materials from Polycondensation of Seed- and Algae Oil-Based Long-Chain Monomers

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Never a failure, always a lesson!

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Publications

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Stempfle, F.; Schemmer, B.; Oechsle, A.-L.; Mecking, S. Thermoplastic polyester elastomers based on long-chain crystallizable aliphatic hard segments. *Polym. Chem.* **2015**, *6*, 7133-7137.

Roesle, P.; Stempfle, F.; Hess, K. S.; Zimmerer, J.; Río Bártulos, C.; Lepetit, B.; Eckert, A.; Kroth, P. G.; Mecking, S. Synthetic polyester from algae oil. *Angew. Chem. Int. Ed.* **2014**, *53*, 6800-6804.

Stempfle, F.; Ritter, B. S.; Mülhaupt, R.; Mecking, S. Long-chain aliphatic polyesters from plant oils for injection molding, film extrusion and electrospinning. *Green Chem.* **2014**, *16*, 2008-2014.

Stempfle, F.; Ortmann, P.; Mecking, S. Which polyesters can mimic polyethylene? *Macromol. Rapid Commun.* **2013**, *34*, 47-50.

Patent application: EP 2695901 A1 (10.08.2012): Aliphatic long-chain polycondensates, Inventor: Mecking, S.; Stempfle, F.; Applicant: BASF SE.

Publications related to this work:

Witt, T.; Stempfle, F.; Roesle, P.; Häußler, M.; Mecking, S. Unsymmetrical α,ω-difunctionalized long-chain compounds via full molecular incorporation of fatty acids. *ACS Catalysis* **2015**, *5*, 4519-4529.

Christl, J. T.; Roesle, P.; Stempfle, F.; Müller, G.; Caporaso, L.; Cavallo, L.; Mecking, S. Promotion of selective pathways in isomerizing functionalization of plant oils by rigid framework substituents. *ChemSusChem* **2014**, *7*, 3491-3495.

Busch, H.; Stempfle, F.; Heß, S.; Grau, E.; Mecking, S. Selective isomerization-carbonylation of a terpene trisubstituted double bond. *Green Chemistry* **2014**, *16*, 4541-4545.

Christl, J. T.; Roesle, P.; Stempfle, F.; Wucher, P.; Göttker-Schnetmann, I.; Müller, G.; Mecking, S. Catalyst activity and selectivity in the isomerizing alkoxycarbonylation of methyl oleate. *Chem. Eur. J.* **2013**, *19*, 17131-17140.

Stempfle, F.; Roesle, P.; Mecking, S. Long-chain polyesters via chemical catalytic conversions of fatty acid esters. *ACS Symp. Ser.: Biobased Monomers, Polymers and Materials* (Eds.: Richard A. Gross, Patrick B. Smith), **2012**, *1105*, 151-163.

Chikkali, S.; Stempfle, F.; Mecking, S. Long-chain polyacetals from plant oils. *Macromol. Rapid Commun.* **2012**, *33*, 1126-1129.

Oral and Poster Presentations:

Stempfle, F.; Ritter, B. S.; Roesle, P.; Mülhaupt, R.; Mecking, S. Plant-oil based linear long-chain aliphatic polyesters for injection molding, film extrusion and electrospinning; Poster presentation at the **7th Workshop on Fats and Oils as Renewable Feedstock for the Chemical Industry** in Karlsruhe, March 2014.

Stempfle, F.; Witt, T.; Roesle, P.; Christl, J. T.; Heckler, I.; Ortmann, P.; Müller, G.; Mecking, S. Selective conversion of plant oils to chemicals and polymers with full molecular feedstock utilization; Oral presentation at the **GDCh Wissenschaftsforum Chemie** in Darmstadt, Sept. 2013.

Stempfle, F.; Roesle, P.; Christl, J. T.; Witt, T.; Müller, G.; Mecking, S. Monomer generation and synthesis of linear long-chain polycondensates from unsaturated fatty acids by isomerizing alkoxycarbonylation; Oral presentation, as well as poster presentation at the **Gordon Research Conference on Green Chemistry** in Barga (Italy), July 2012.

Stempfle, F.; Ortmann, P.; Quinzler, D.; Roesle, P.; Trzaskowski, J.; Mecking, S. Aliphatic polyesters via catalytic carbonylation and metathesis; Poster presentation at the **Forum of Molecular Catalysis 2011** in Heidelberg, July 2011.

Stempfle, F.; Quinzler, D.; Heckler, I.; Mecking, S. Linear semicrystalline polycondensates from plant oils; Oral presentation at the **4th Workshop on Fats and Oils as Renewable Feedstock for the Chemical Industry** in Karlsruhe, March 2011.

Zusammenfassung

In den letzten Jahrzehnten hat auf dem Gebiet der Kunststoffe eine enorme Entwicklung stattgefunden, so dass diese aus unserem Alltag nicht mehr wegzudenken sind. Die Herstellung erfolgt dabei überwiegend auf Basis fossiler Rohstoffe, wie zum Beispiel Erdöl oder Erdgas. Insbesondere thermoplastische Polymere, die neben Duroplasten und Elastomeren zu den im Alltag am meisten verwendeten Kunststoffen zählen, werden fast ausschließlich aus nicht erneuerbaren, fossilen Rohstoffen hergestellt. Vor dem Hintergrund der begrenzten Verfügbarkeit dieser fossilen Rohstoffe und um Ressourcen zu schonen ist mittel- bis langfristig die Entwicklung alternativer Herstellungsverfahren auf der Grundlage von nachwachsenden Ressourcen wünschenswert.

Aus chemischer Sicht sind für die Synthese von linearen Polymeren aus nachwachsenden Rohstoffen vor allem pflanzliche Fettsäuren von Interesse. Diese enthalten neben langen kristallisierbaren, aliphatischen Segmenten verschiedene funktionelle Gruppen, die unter anderem zur Herstellung linearer, teilkristalliner Polyester oder Polyamide verwendet werden können. Solch langkettige, aliphatische Polykondensate sind von besonderem Interesse, da beispielsweise durch den linearen Einbau der langen Kohlenwasserstoffketten kristalline Polyester mit hohen Schmelzpunkten (T_m > 100 °C) erhalten werden können. Neben biotechnologischen Verfahren, wie zum Beispiel der ω-Oxidation, sind für die Synthese der hierfür benötigten langkettigen, α,ω-bifunktionellen Monomere, vor allem chemisch-synthetische Umsetzungen von Interesse.

Im Rahmen dieser Arbeit konnten durch eine Sequenz aus Selbstmetathese, Veresterung und anschließende Hydrierung der vorhandenen Doppelbindung, ausgehend von Öl- bzw. Erucasäure, sowohl der C_{18}- als auch der C_{26}-Diester hergestellt werden (**Abb. 1**).

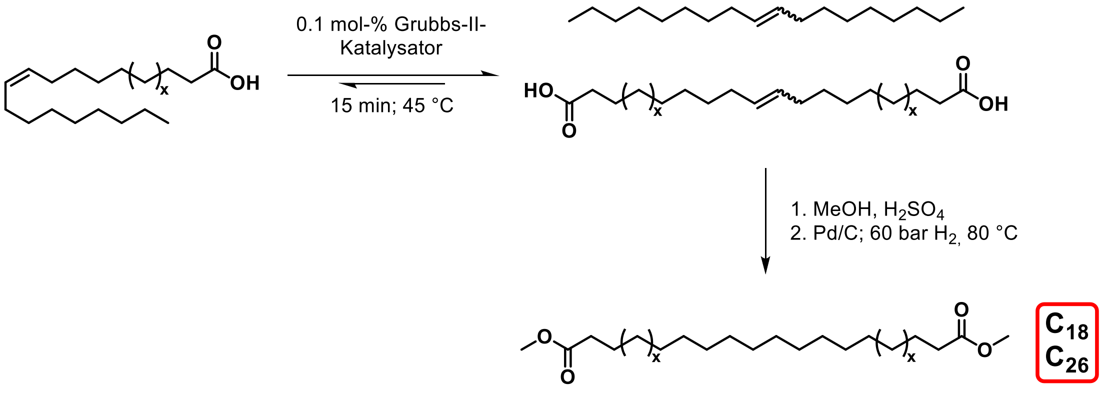


Abb. 1: Synthese von Dimethyl-1,18-octadecandioat und Dimethyl-1,26-hexacosandioat durch eine Sequenz aus Selbstmetathese, Veresterung und katalytische Hydrierung der vorhandenen Doppelbindung.

Besonderes Augenmerk galt dabei der Unterdrückung der Isomerisierung der Doppelbindung während der Metathesereaktion. Diese unerwünschte Nebenreaktion, welche sowohl zu kürzeren als auch zu längeren difunktionellen Verbindungen führt, konnte durch Optimierung der Reaktionsbedingungen und eine geeignete Wahl des Ausgangsmaterials vollständig unterdrückt werden, so dass beide Diester in einer Reinheit von ≥ 99 % erhalten wurden. Anschließende Reduktion mit $LiAlH_4$ oder katalytische Hydrierung führte zu den entsprechenden langkettigen Diolen.

Die auf diese Art und Weise erhaltenen langkettigen α,ω-funktionalisierten Verbindungen wurden anschließend in Polykondensationsreaktionen zu Poly[1,18-octadecandiyl-1,18-octadecandioat] (**PE-18.18**) und Poly[1,26-hexacosandiyl-1,26-hexacosanedioat] (**PE-26.26**) umgesetzt. Beide Polyester besitzen ein zahlenmittleres Molekulargewicht von mehreren 10^4 g mol^{-1} und zeigen im Vergleich zu kommerziell erhältlichen, aliphatischen Polyestern hohe Schmelzpunkte von T_m = 100 °C für **PE-18.18** bzw. T_m = 114 °C für **PE-26.26**.

Des Weiteren konnte in dieser Arbeit gezeigt werden, dass durch Selbstmetathese von einfach ungesättigten Fettalkoholen und anschließende Isomerisierung der Doppelbindung selektiv ω-Hydroxyaldehyde aus den Enolen erhalten werden können, die über traditionelle organische Synthese nur sehr schwer zugänglich sind (**Abb. 2**).

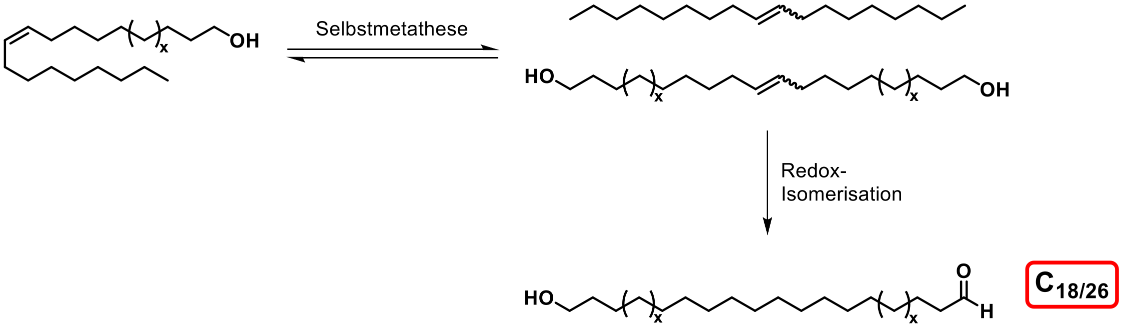


Abb. 2: Selbstmethathese und Redox-Isomerisierung von Oleylalkohol (x=1) und Erucylalkohol (x=5).

Selektive Oxidation des Aldehyds ermöglicht zudem den Zugang zu langkettigen ω-Hydroxycarbonsäureestern, die unter anderem als Monomere für eine AB-Typ Polykondensation verwendet werden können. Ausgehend von Undec-10-en-1-ol, das durch thermische Zersetzung von Rizinusöl gewonnen wird, kann in gleicher Art und Weise der C_{20} ω-Hydroxycarbonsäureester erhalten werden. Auf Basis dieser unsymmetrischen AB-Monomere wurde im Rahmen der vorliegenden Arbeit sowohl Poly[ω-hydroxyl octadecansäure] (**PE-18**) als auch Poly[ω-hydroxyl eicosansäure] (**PE-20**) hergestellt. Beide langkettigen, aliphatischen Polyester zeigen ein zahlenmittleres Molekulargewicht von mehreren 10^4 g mol^{-1} und ebenfalls hohe Schmelzpunkte von über 100 °C.

Bei den bisher vorgestellten Syntheserouten zu langkettigen α,ω-funktionalisierten Verbindungen wird jedoch immer nur ein Teil der Fettsäurekette in das entsprechende Polymer überführt, da die Fettsäure an der reaktionsfreudigen Doppelbindung in der Mitte des Moleküls gespalten wird. Um den Rohstoff möglichst effizient zu nutzen ist eine Funktionalisierung am Kettenende erforderlich. Dies gelingt beispielsweise durch die isomerisierende Alkoxycarbonylierung. Bei dieser Reaktion wird die interne Doppelbindung isomerisiert und am Kettenende selektiv mit Kohlenmonoxid und einem

Alkohol zum endständigen Ester umgesetzt. Ausgehend von Methyloleat bzw. Methylerucat können so sowohl Dimethyl-1,19-nonadecanedioat als auch Dimethyl-1,23-tricosanedioat in einer Reinheit von ≥ 99 %. dargestellt werden. Beide Verbindungen wurden im Rahmen dieser Arbeit im Maßstab von über 100 g erhalten und anschließend durch Reduktion mit $LiAlH_4$ oder katalytische Hydrierung in die entsprechenden Diole überführt (**Abb. 3**).

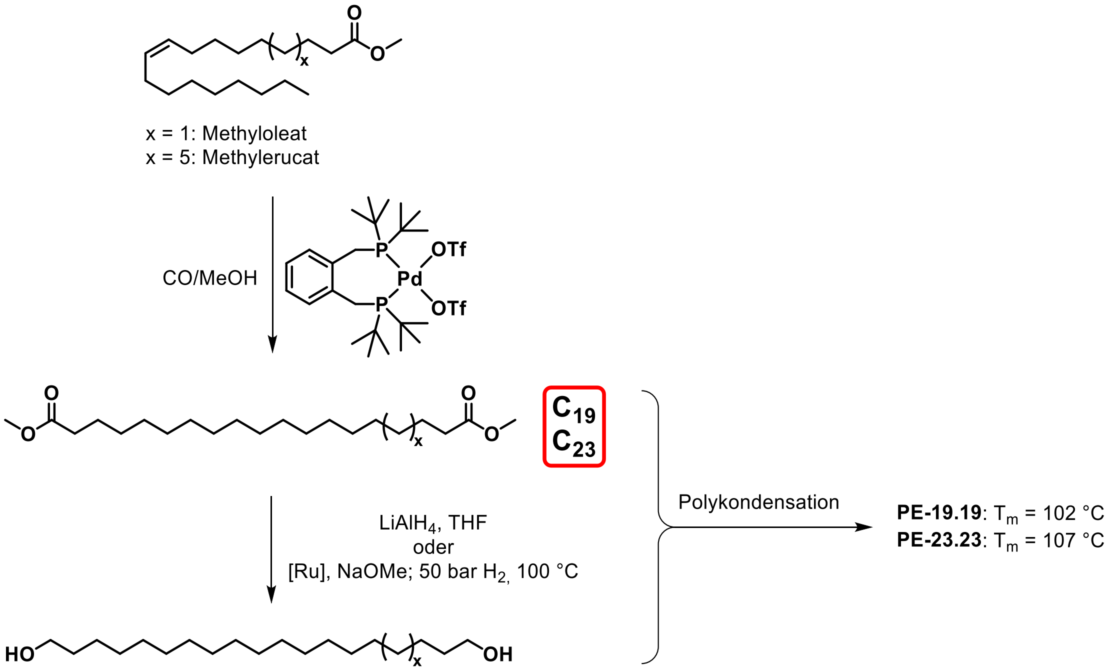


Abb. 3: Synthese von Poly[1,19-nonadecadiyl-1,19-nonadecandioat] (**PE-19.19**) und Poly[1,23-tricosadiyl-1,23-tricosandioat] (**PE-23.23**).

Polykondensation der so erhaltenen langkettigen, α,ω-difunktionalisierten Verbindungen führt zu Poly[1,19-nonadecadiyl-1,19-nonadecandioat] (**PE-19.19**) und Poly[1,23-tricosadiyl-1,23-tricosandioat] (**PE-23.23**). Nach Optimierung der Polykondensationsbedingungen sind nun beide Polyester im Maßstab von mehr als 10 g pro Ansatz mit einem zahlenmittleren Molekulargewicht von über 3,0 × 10^4 g mol^{-1} verfügbar. Die Schmelztemperaturen liegen dabei bei T_m = 102 °C für **PE-19.19** und T_m = 107 °C für **PE-23.23**. Erste Untersuchungen der Materialeigenschaften dieser neuartigen Polymere an spritzgegossenen Prüfkörpern zeigen ein E- Modul von ungefähr 400 MPa bei einer Bruchdehnung von über 600 %. Darüber hinaus deuten erste Versuche darauf hin, dass diese neuartigen Materialien eine verbesserte hydrolytische Stabilität, sowohl in sauren als auch alkalischen Medien, aufweisen.

Im Rahmen der vorliegenden Arbeit konnte zudem herausgearbeitet werden, dass solch langkettige, α,ω-funktionalisierte Verbindungen auch als kristalline Hartsegmente in thermoplastischen Elastomeren verwendet werden können. Durch Polykondensation von Dimethyl-1,23-tricosandioat und 1,23-Tricosandiol zusammen mit OH-terminiertem Polytetrahydrofuran als Weichsegment wurden Polyester-Polyether Copolymere mit einem zahlenmittleren Molekulargewicht von bis zu

$6{,}0 \times 10^4$ g mol^{-1} erhalten. In Abhängigkeit von der Zusammensetzung, sowie des Molekulargewichts des Polytetrahydrofuran-Weichsegments, zeigen diese rein aliphatischen, thermoplastischen Elastomere Schmelzpunkte zwischen 30 und 96 °C. Erste Untersuchungen der Materialeigenschaften dieser neuartigen Polymere an spritzgegossenen Prüfkörpern belegen, dass durch die langen, kristallisierbaren Kohlenstoffketten physikalische Vernetzung erzielt werden kann, die bei ausreichend hohem Anteilen der langkettigen aliphatischen Monomerkomponenten zu elastomerem Verhalten, mit gutem Rückstellvermögen und einer Bruchdehnung von bis zu 870 %, führt.

Üblicherweise werden jedoch für die hier vorgestellten chemisch-synthetischen Umsetzungen pflanzliche Fettsäuren als Rohstoffquelle genutzt. Im letzten Teil dieser Arbeit konnte gezeigt werden, dass auch Algen, trotz ihrer signifikant anderen Zusammensetzung, welche die Katalysatoren deaktivieren könnte, als geeignetes Ausgangsmaterial verwendet werden können. Nach Extraktion der einzelligen Kieselalge *Phaeodactylum tricornutum* wurde das erhaltene Algenöl über die isomerisierende Alkoxycarbonylierung in eine Mischung aus langkettigen, α,ω-funktionalisierten Diestern unterschiedlicher Kettenlänge (C$_{17}$ und C$_{19}$) überführt und anschließend durch Reduktion mit LiAlH$_4$ in die entsprechenden Diole umgewandelt (**Abb. 4**).

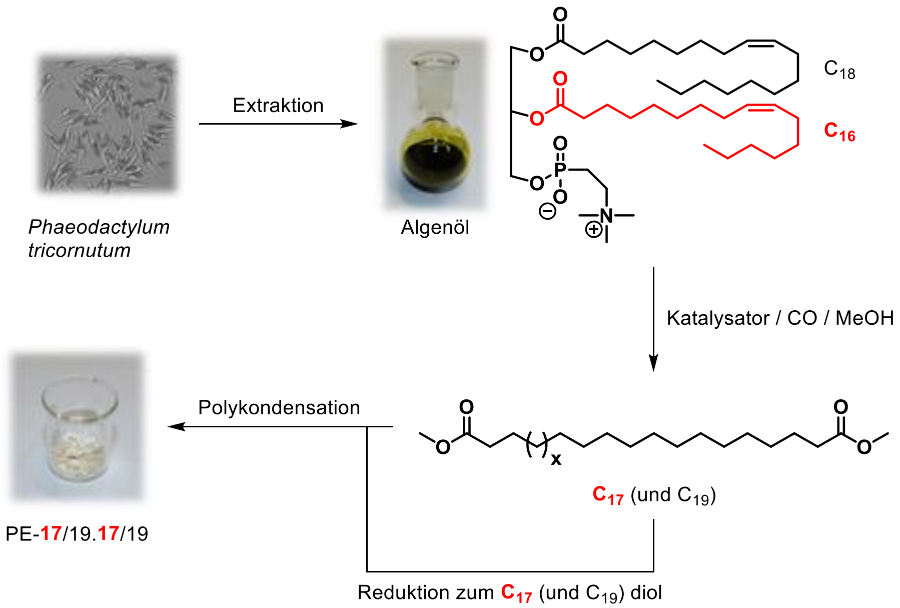


Abb. 4: Syntheseroute zu langkettigen, aliphatischen Polyestern auf Basis von Algenöl.

Die auf diese Art und Weise hergestellten Monomere konnten in der für Polykondensationen erforderlichen Reinheit von ≥ 99 % isoliert werden und wurden anschließend zur Herstellung eines gemischten Polyesters **PE-17/19.17/19** auf Basis von Algenöl verwendet. Bei einem zahlenmittleren Molekulargewicht von mehreren 10^4 g mol^{-1} besitzt dieser gemischte Polyester einen Schmelzpunkt von 99 °C und fügt sich somit hervorragend in die Reihe der Schmelzpunkte anderer, langkettiger, Polyester mit regelmäßiger Struktur ein.

Table of contents

List of abbreviations

Equipment and methods

DMA	Dynamic Mechanical Analysis
DSC	Differential Scanning Calorimetry
GC	Gas Chromatography
GPC	Gel Permeation Chromatography
NMR	Nuclear Magnetic Resonance
WAXD	Wide-angle X-ray Diffraction

NMR-Spectroscopy

br	Broad
s	Singlet
d	Doublet
dd	Doublet of doublets
t	Triplet
q	Quartet
m	Multiplet
$^nJ_{xy}$	Coupling constant of atom X and Y over n bounds
ppm	Parts per million
δ	Chemical shift in ppm

Compounds

acac	Acetylacetonate
biphephos	6,6'-[(3,3'-Di-*tert*-butyl-5,5'-dimethoxy-1,1'-biphenyl-2,2'-diyl)bis(oxy)] bis(dibenzo[*d*,*f*][1,3,2]dioxaphosphepin)
coe	Cyclooctene
dppe	1,2-Bis(diphenylphosphino)ethane
dtbpx	1,2-Bis[(di-*tert*-butylphosphino)methyl]benzene
FAME	Fatty acid methyl ester
P^P	Diphosphine
PBS	Phosphate buffered saline
PE-X.Y	Polyester, that is derived from C_x-diol and C_y-diacid
PET	Poly(ethylene terephthalate)
ROP	Ring Opening Polymerization

Other abbreviations

DP_n	Degree of polymerization = M_n/M_0 (M_0 molecular weight of the repeat unit)
G`	Storage modulus
G``	Loss modulus
mol-%	Mol fraction
M_n	Number average molecular weight
M_w	Weight average molecular weight
M_w/M_n	Molecular weight distribution
p	Pressure
T	Temperature
T_c	Crystallization temperature
T_m	Melting temperature
wt.-%	Percentage by mass

1 General introduction

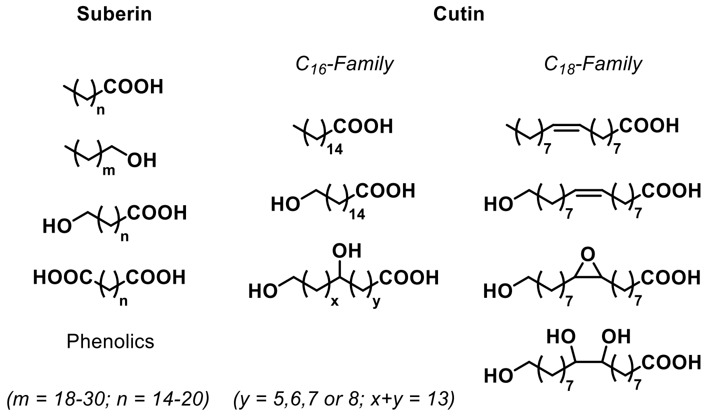
For the largest part, synthetic polymers possess an aliphatic backbone structure. In terms of scale the most prominent examples are polyolefins. But also polycondensates like polyesters and polyamides are largely aliphatic. In technically relevant polyesters and polyamides, the aliphatic segments are relatively short, typically amounting to six atoms or shorter linear carbon chains. Thus, the physical and applications properties are often dominated by the polycondensates' functional groups. For example, the advantageously high modulus and heat distortion temperature of polyamide-6,6 arise from hydrogen bonds between the amide groups. However, an intermediate situation in which both a polycondensate nature as well as an aliphatic chain nature contribute substantially, is of interest in its own right. For example, other than low-density polyethylene (LDPE), polyesters can allow for hydrolytic degradability and enable applications like disposable bags for compostable waste. In order to achieve sufficient melting and crystallization points, however, aromatic repeat units are required and the commercial products are mixed aromatic-aliphatic polyesters. In principle, such higher melting points can also be achieved in all-aliphatic polyesters by virtue of longer-chain aliphatic repeat units, that crystallize via van-der-Waals interactions between the hydrocarbon segments, akin to polyethylene.

Polyesters with longer chain linear aliphatic repeat units have been studied early on, already in the pioneering work of Carothers.[1] The relationship between monomer chain length and melting points was studied in much detail. Other than this, longer-chain difunctional monomers and their corresponding polymers have received comparatively little attention. This can be traced to the lack of viable routes to access these monomers in a more practical fashion than the multistep traditional organic syntheses employed for the preparation of these model polymers.

In principle, fatty acids are an attractive substrate to consider for this purpose in that they contain longer aliphatic segments -$(CH_2)_n$- as a structural feature along with a terminal functional group. To illustrate the problem of their conversion to polycondensation monomers, the existing application of fatty acid derivatives as cross-linkers in polyurethanes is instructive. In this case, a multiple mid-chain functionalization, e.g. via epoxidation of the double bonds and subsequent hydrolysis, affords multifunctional molecules.[2] As another example, branched 'dimer fatty acids' as difunctional monomers are produced by a mid-chain dimerization of two molecules of unsaturated fatty acids.[3,4,5] However, to obtain crystallizable linear α,ω-difunctional monomers, other approaches like a selective terminal functionalization of the fatty acid chain are required. Recent advances in catalytic conversions of plant oils provide solutions to this problem. This encourages to bridge the gap between semicrystalline polyolefins and traditional polycondensates.

1.1 Sources of monomers

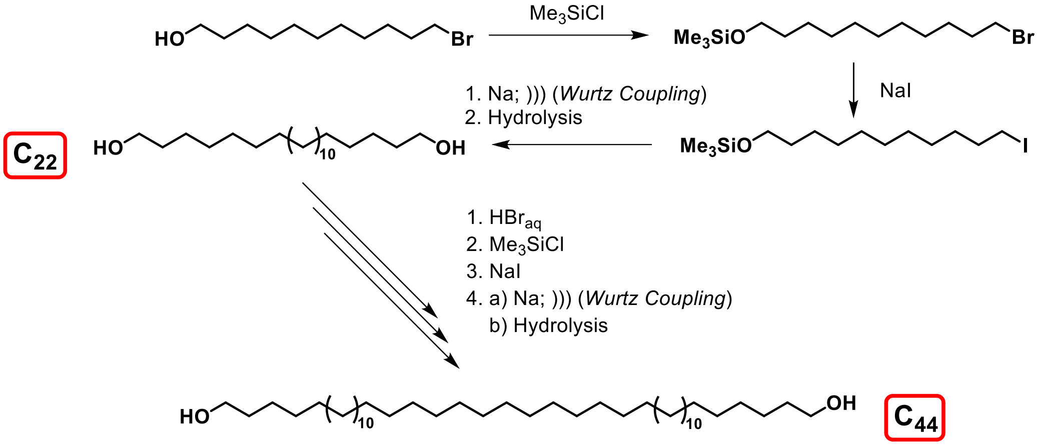
For the synthesis of long-chain aliphatic polyesters polycondensation monomers with appropriate amounts of methylene segments are required. Traditionally, these linear long-chain difunctional compounds are prepared via sequential build-up starting from shorter chain building blocks. An interesting alternative to these multistep syntheses is a selective terminal functionalization of fatty acid derivatives, which already contain linear long chain crystallizable segments. A number of such straight-chain compounds actually also occur naturally. Aliphatic long-chain dicarboxylic acids as well as ω-hydroxy carboxylic acids for example are building blocks of naturally occurring polyesters like cutin and suberin in cork (**Scheme 1.1**).[6,7] Nevertheless these natural resources normally are not used to recover these compounds, as their purity is often low and removal of other contaminants is extremely difficult. Hence these polycondensation monomers have often been prepared via classical organic synthesis.



Scheme 1.1: Structure of the major repeat units of suberin and cutin.[6]

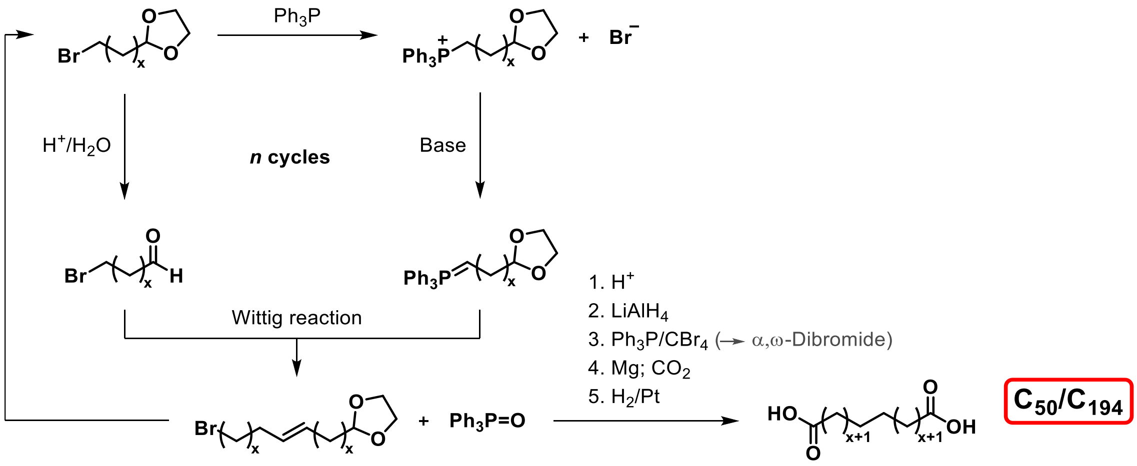
1.2 Classical organic synthesis

A range of laboratory scale multistep synthesis schemes starting from smaller building blocks, often applying elaborated protection and deprotection steps, have been developed in the past. Syntheses of long-chain α,ω-functionalized compounds for instance can be achieved by coupling of two shorter-chain fragments; e.g. docosane-1,22-diol can be synthesized in three steps from commercially available 11-bromoundecan-1-ol (**Scheme 1.2**).[8]



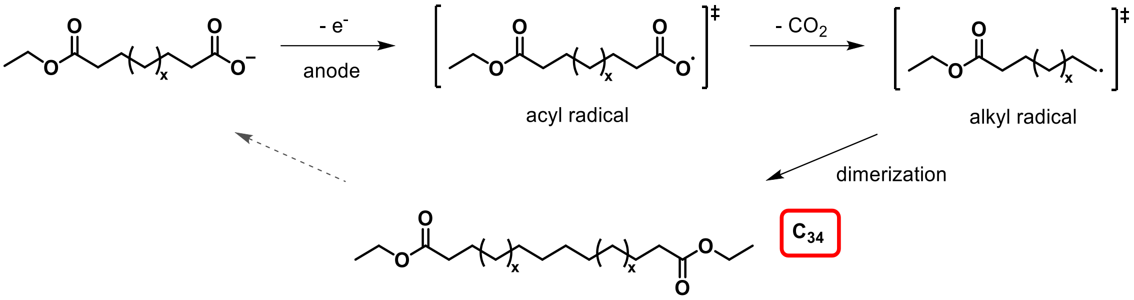
Scheme 1.2: Multi-step synthesis of docosane-1,22-diol and tetratetracontane-1,44-diol.[8]

By a repeated sequence of mono-bromination of the C_{22} diol and coupling to double the original chain length, an extension up to 44 carbon atoms was possible, yielding tetratetracontane-1,44-diol.[8,9,10] Even longer α,ω-functionalized compounds have been obtained by a multi-step procedure developed for the synthesis of very long chain alkanes[11] and functionalized derivatives thereof.[12] Based on an iterative sequence involving a coupling step through Wittig olefination of an aldehyde, straight chain aliphatic dicarboxylic acids containing from 48 up to 192 methylene groups were generated (**Scheme 1.3**).



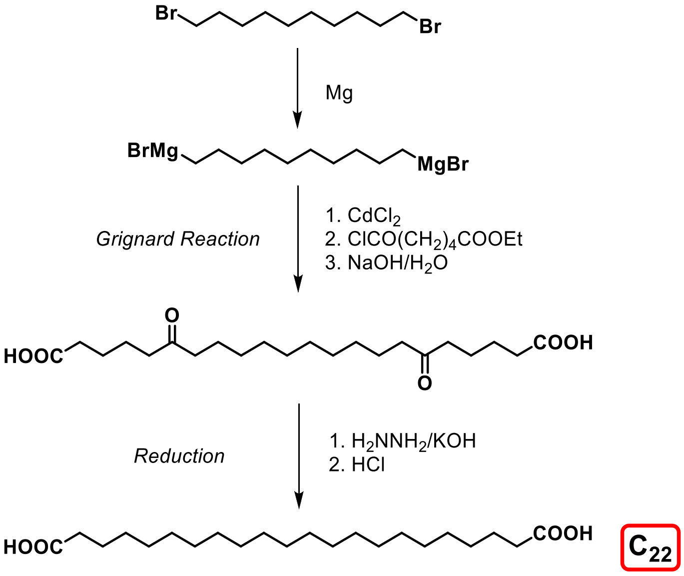
Scheme 1.3: Multi-step synthesis[a] of pentacontane-1,50-dioic acid (n = 2) and tetranonacontahectane-1,194-dioic acid (n = 4).[12]
[a] The first reaction sequence starts with x = 10, whereas n is the number of cycles applied.

Another useful coupling protocol to linear long-chain α,ω-functionalized compounds is Kolbe electrolysis.[13] Anodic decarboxylation of dicarboxylic acid (half-)esters gives access to radicals for dimerization and coupling, leading to the higher homologues of the dicarboxylic acids (Brown-Walker coupling).[14,15,16] Starting from sodium ethyl sebacate, the linear long-chain aliphatic C_{34} diester can be obtained via two subsequent electrolysis steps (**Scheme 1.4**). As a side note, this synthetic method has been also applied to the methyl ester of the C_{36} dimer fatty acid (isomeric mixture), which was coupled to yield a mixture of branched C_{70} diesters.[17]



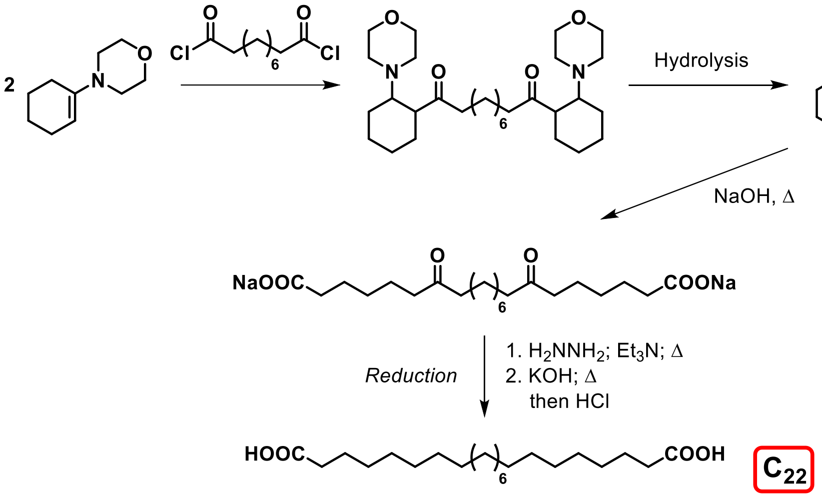
Scheme 1.4: Electrolytic synthesis of diethyl tetratriacontane-1,34-dioate (2 cycles with x = 4).[15]

Further approaches have been developed to extend the chain length of α,ω-functionalized compounds. Starting from aliphatic α,ω-dihalides, long-chain dicarboxylic acids with up to 22 carbon atoms have been prepared by metal-catalyzed coupling reactions with short-chain α,ω-ester acid chlorides.[18] In this way, for example, 1,10-dibromodecane can be extended to yield docosane-1,22-dioic acid (**Scheme 1.5**). Even longer chain dicarboxylic acid esters, namely dimethyl-tetracosane-1,24-dioate and diethyl tetracontane-1,30-dioate, can be prepared by coupling with iodo-substituted carboxylic acid esters of the appropriate chain lengths.[19]



Scheme 1.5: Chain-extension of 1,10-dibromodecane via Grignard coupling with short-chain α,ω-ester acid chlorides.[18]

An alternative route to docosane-1,22-dioic acid is a chain extension of decane-1,10-dioic acid by twelve carbon atoms via C-C scission of a cyclic malonic ester as the key step (**Scheme 1.6**).[20] This chain-extension approach has been applied to different α,ω-dicarboxylic acids.[21] Moreover by both, increasing the ring size of the enamine and multiple application of this reaction sequence, chains of considerable length can be constructed.[22,23,24] In this way Hünig *et al.* for example synthesized linear α,ω-dicarboxylic acids with up to 56 carbon atoms. They already pointed out the decreasing solubility of the products as a limiting factor for this synthetic pathway.[24] Nevertheless, Wakselman and coworkers could even achieve heptacontane-1,70-dioic acid by combination of these chain extension reactions.[25]



Scheme 1.6: Chain-extension of decane-1,10-dioic acid to docosane-1,22-dioic acid.[20]

Many further examples of such multi-step approaches to α,ω-long-chain compounds have been reported.[26-35] While they are elegant in providing even components with a very large number of carbon atoms precisely, they are very tedious and rather inefficient as a source of monomers for purposes others than model polymers on a small scale.

1.3 Plant-oil fatty acids as a source of mid-chain monomers

These classical organic syntheses still remain tedious and inefficient. Purification and isolation of the long-chain compounds become more and more difficult, as the chain length increases. Differences in physical properties between starting material, desired product and possible side-products vanish, eventually making a separation difficult. Moreover, although conversions of the single reaction steps might be convincing, the yield of the desired final product referred relative to the starting material utilized is often limited. Alternative approaches have emerged utilizing plant-oil derived fatty acids, as these substrates already contain linear long-chain hydrocarbon segments. In this context, it is instructive to briefly review existing routes to shorter, medium chain monomers from fatty acids. Some pathways to such polycondensation monomers (with numbers of carbon atoms ranging up to 13) from unsaturated fatty acids are already established industrially. As the most prominent starting material ricinoleic acid, the major component of castor oil, has been used since many years. Undecenoic acid for example is obtained via thermal rearrangement with chain cleavage.[36] Further addition of hydrobromic acid and addition of ammonia yields 11-aminoundecanoic acid, the starting material for nylon-11. Likewise, sebacic acid, which is used for nylon-6.10 synthesis, can be generated by cleavage under strongly basic conditions (**Figure 1.1**).[37]

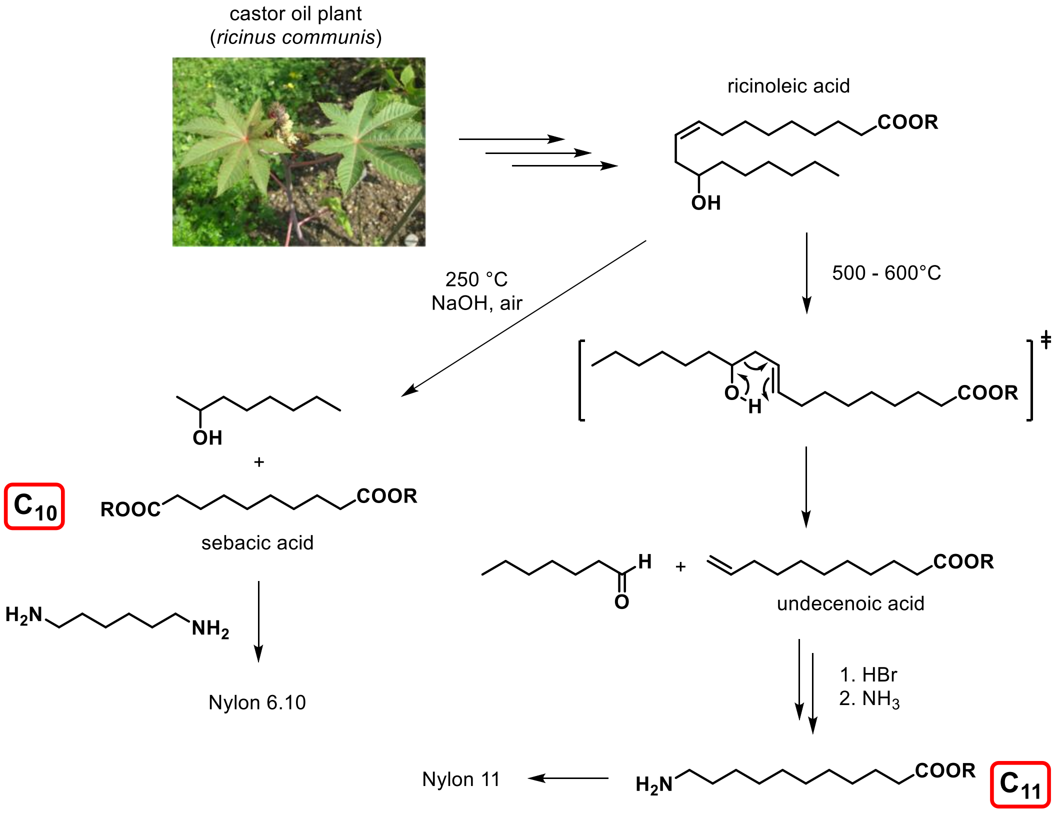
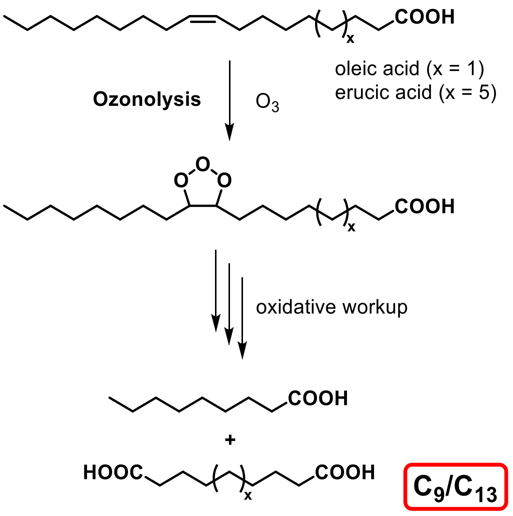


Figure 1.1: Mid-chain length monomers and polyamides based on ricinoleic acid.

Both of these routes require a hydroxy substituted unsaturated fatty acid, of which ricinoleic acid is the only practically available example. Castor oil, consisting mainly of ricinoleic acid (85-95 %), is currently produced with an annual capacity of about 600,000 tons.[38] However, it is significantly more costly (ca. double the price) than other plant oils like soybean, palm or rapeseed oil. Moreover, in the transformations described above only one side of the fatty acid chain with respect to the double bond is incorporated and stoichiometric amounts of less valuable byproducts are formed. These arguments also apply to ozonolysis, which converts monounsaturated fatty acids to α,ω-diacids. In this way several thousand tons of 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 (**Scheme 1.7**).[39,40]

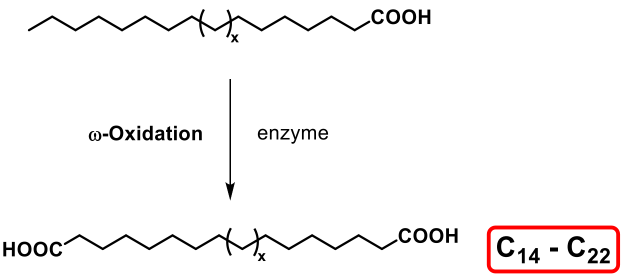


Scheme 1.7: Synthesis of azelaic and brassylic acid by ozonolysis of oleic acid and erucic acid, respectively, both giving pelargonic acid as a byproduct.[39]

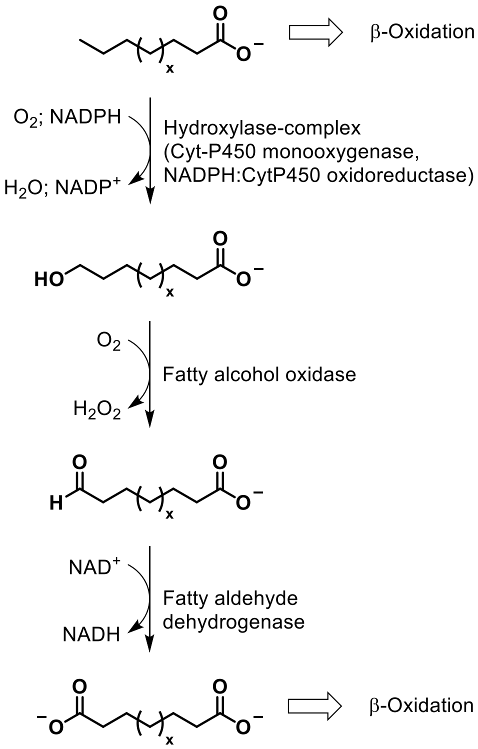
To employ the potential of the linear long-chain hydrocarbon segments and also in order to utilize the feedstock most efficiently, a full incorporation of the entire fatty acid chain into linear long-chain α,ω-functionalized compounds is desirable. Biotechnological transformations provide a possible approach to this challenge.

1.3.1 Biotechnological ω-oxidation

Certain yeasts strains, e.g. *Candida tropicalis*, *Candida maltosa* and *Yarrowia lipolytica* are able to oxidize terminal aliphatic carbons to carboxylic acids. This ω-oxidation enables the conversion of fatty acids and their derivatives to long-chain dicarboxylic acids (**Scheme 1.8**).[41,42,43]



Scheme 1.8: Enzymatic ω-oxidation of fatty acids.



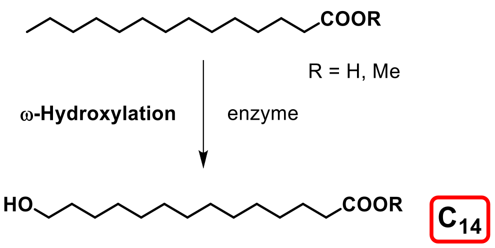
Scheme 1.9: Mechanism of terminal oxidation of fatty acids.[43]

Linear aliphatic diacids with the same number of carbon atoms as the fatty acid starting material, that is an even number usually in the range from 14 to 22, can be obtained. The first step of this biotechnological transformation is catalyzed by a hydroxylase complex and involves a terminal oxidation of the fatty acid to a primary alcohol (**Scheme 1.9**). In a second step the alcohol is oxidized by a fatty alcohol oxidase to the corresponding aldehyde, which is subsequently converted to the carboxyl group of the corresponding diacid.[44] Given that the fatty acids, as well as dicarboxylic acids, can be metabolized further via the β-oxidation pathway to produce energy, an enrichment of the α,ω-functionalized target compound is only possible by blocking these degradation pathways, either by deletion of genes involved in this metabolic oxidation,[45,46] or by manipulation of transport processes within the cell.[47] As a trade-off an additional, often costly carbon source like glucose is necessary to maintain the energy supply. Further optimization of the biocatalyst was achieved via overexpression of enzymes. Amplification of the Cyt-P450 monooxygenase (CYP) and NADPH:Cyt oxidoreductase (CPR) genes in *Candida tropicalis* involved in the ω-oxidation pathway leads to a 30 % increase in productivity compared to the β-oxidation blocked wildtype (**Table 1.1**; entries 1 and 2).[48,49]

Table 1.1: Maximum product concentration (C_{Max}) and maximum production rate of dicarboxylic acid (R_{Max}) in ω-oxidation.

entry	Strain	Substrate	C_{Max}	R_{Max}	Ref.
1	C. tropicalis (AR40)	95 % methyl myristate (14:0)	150 g L^{-1} in 92 h	1.63 g L^{-1} h^{-1}	[48]
2	C. tropicalis (H5343)	95 % methyl myristate (14:0)	115 g L^{-1} in 92 h	1.25 g L^{-1} h^{-1}	[48]
3	C. tropicalis (AR40)	95 % methyl myristate (14:0)	145 g L^{-1} in 118 h	1.47 g L^{-1} h^{-1}	[48]
4	C. tropicalis (AR40)	95 % methyl palmitate (16:0)	94 g L^{-1} in 118 h	0.80 g L^{-1} h^{-1}	[48]
5	C. tropicalis (AR40)	95 % methyl stearate (18:0)	71 g L^{-1} in 118 h	0.60 g L^{-1} h^{-1}	[48]
6	C. tropicalis (ATCC20962)	oleic acid (18:1)	18 g L^{-1} in 72 h	0.25 g L^{-1} h^{-1}	[50]
7	C. tropicalis (ATCC20962)	erucic acid (22:1)	14 g L^{-1} in 72 h	0.20 g L^{-1} h^{-1}	[50]

The productivity of these biotechnological transformations strongly depends on a variety of different parameters (e.g. medium composition, availability of oxygen, pH-value, temperature and emulsification of hydrophobic substrates) and has to be optimized during bioprocess engineering. Key features of selected optimized fermentation approaches for the microbial transformation of long-chain dicarboxylic acids with different chain lengths are summarized in **Table 1.1**. Remarkably, substrates with shorter chain length can be converted with higher efficiency when compared to long-chain substrates (**Table 1.1**; entries 3-5). Moreover it could be demonstrated that the position of the double bond in unsaturated fatty acids is maintained (**Table 1.1**; entries 6 and 7). Thus, also unsaturated α,ω-functionalized diacids can be prepared.[50]



Scheme 1.10: ω-Hydroxylation of myristic acid and methyl myristate.[51]

A related transformation of fatty acid substrates is ω-hydroxylation, introducing a terminal hydroxy group at the unsubstituted hydrocarbon chain end. Applying modified yeast strains the

14-hydroxytetradecanoic acid can be obtained with yields of 174 g L^{-1} with less than 5 % formation of the corresponding dicarboxylic acid after 148 h of biotransformation (**Scheme 1.10**).[51] A key requirement is the elimination of enzymes that oxidize the alcohol group in the second step of the ω-oxidation pathway (cf. **Scheme 1.9**). As demonstrated by Gross and coworkers this can be achieved by genetically modifying a *Candida tropicalis* strain in 16 genes. Such engineered strains are capable of converting a range of fatty acids with various chain lengths (14:0; 16:0; 18:0; 18:1; 18:2) to the desired unsymmetrical compounds, which can serve amongst others as AB-type monomers for polyester synthesis.[51,52]

A crucial issue in all these biotransformations is the downstream processing, i.e. separation and purification of the products from the fermentation broth. Mechanical, thermal or chemical separation methods have to be adapted to the upstream bioconversion process, just as much as to further utilization of the obtained compounds.[53] As high purities of the products are required for their application as polycondensation monomers, the latter point is especially important.

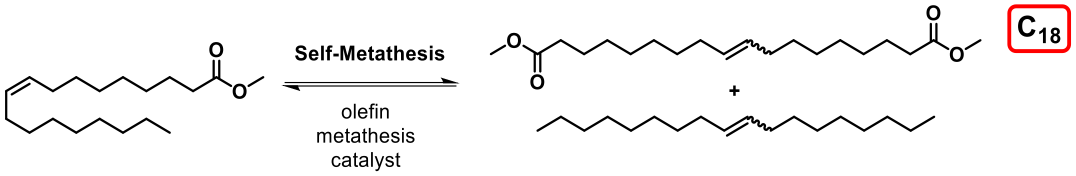
Due to the classification of *Candida tropicalis* as a pathogenic microorganism,[54] current research efforts are also focused on the utilization and optimization of non-pathogenic microorganisms such as *Yarrowia lipolytica* or *Saccharomyces cerevisiae*.[43] Currently, several companies are active in the microbial production of medium- and long-chain dicarboxylic acids from fatty acids. This technology has been pioneered amongst others by Cognis, [55,56] but most producing companies using this technology are located in China (e.g. Cathay Industrial Biotech and Shandong Hilead Biotechnology).

1.3.2 Olefin metathesis

An entirely chemical-synthetic approach to linear long-chain α,ω-functionalized compounds is provided by olefin metathesis. In the last two decades major improvements have been achieved in metathesis catalyst performance, and olefin metathesis has evolved as a powerful tool for oleochemistry.[57-62] Metathesis products like unsaturated diacids, diesters, or mixed α,ω-functionalized compounds in principle can be used for polycondensation conversions after hydrogenation of the carbon-carbon double bonds. However, as double bond isomerization[63] is a generic issue in olefin metathesis and ultimately will result in the formation of α,ω-difunctional compounds of various chain-length, which likely cannot be separated completely, this side reaction is a crucial issue for the generation and isolation of well-defined α,ω-functionalized polycondensation monomers in pure form (> 99 %).

Self-metathesis reactions

An early example of self-metathesis of unsaturated fatty esters into mono-unsaturated hydrocarbons and α,ω-diesters was reported by van Dam *et al.* in 1974.[64] Using $WCl_6/SnMe_4$ as a catalyst system, methyl oleate (and methyl elaidate) were converted to dimethyl-octadec-9-ene-1,18-dioate and octadec-9-ene, reaching equilibrium conversion within a few hours (**Scheme 1.11**).

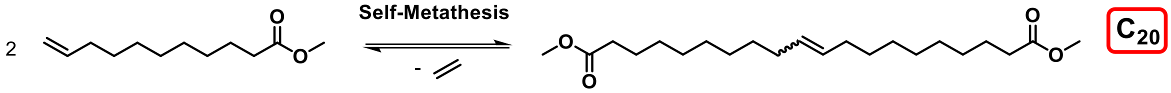


Scheme 1.11: Self-metathesis of methyl oleate.

Subsequently, several other classical *in situ* catalyst systems and also heterogeneous catalysts were found to convert unsaturated fatty acids and oil substrates.[65,66] However, their performance in these reactions is limited due to their (partially) insufficient tolerance toward the substrates' carboxylic acid or ester groups.[59] This issue was advanced with the development of more functional group tolerant, defined metal alkylidene metathesis catalyst precursors.[67,68]

In particular, ruthenium alkylidenes, most prominently $[(PCy_3)_2Cl_2Ru{=}CHPh]$ (Grubbs first generation catalyst) and $[(PCy_3)(\eta\text{-}C\text{-}C_3H_4N_2Mes_2)Cl_2Ru{=}CHPh]$ (Grubbs second generation catalyst) have been found to be very active catalyst precursors. High productivities of up to several 10^5 turnovers have been reported for self-metathesis of methyl oleate, applying these catalyst precursors.[69] Nevertheless, molar conversions are limited (at its best ≈ 50 % in homogeneous solution), since such reactions typically are subjected to thermodynamic control. This limitation can be overcome applying solvent-free self-metathesis of monounsaturated fatty acids. Under these bulk conditions, the diacid products formed during the reaction are not soluble in the reaction medium and precipitate from the mixture. This removal of a product shifts the equilibrium mixture. Thus, conversion of the starting material and yields of the diacid products increase. In this way even carbon numbered, monounsaturated dicarboxylic acids can be obtained.[70] By comparison, self-metathesis of mixtures containing multiple unsaturated fatty acid methyl esters (FAMEs), such as methyl linoleate or methyl linolenate, gives rise to more complex product mixtures, including linear polyenes, monoesters, diesters and cyclopolyenes.[71] This issue becomes even more relevant considering the self-metathesis of common plant oils, which typically contain triglycerides of fatty acids of different chain lengths and, in particular often possess significant amounts of their multiply unsaturated analogues, additionally to the monounsaturated compounds.[72]

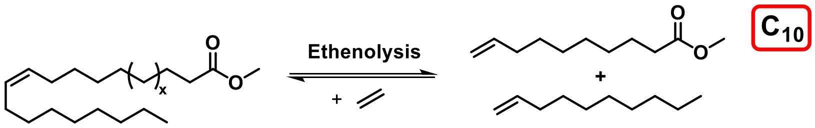
Another potential route to linear α,ω-difunctional compounds is self-metathesis of ω-unsaturated compounds. Self-metathesis of methyl undec-10-enoate, which can be obtained by pyrolysis of methyl ricinoleate from castor oil, for example yields internally unsaturated dimethyl-eicos-10-ene-1,20-dioate (**Scheme 1.12**).[73] By removing the volatile by-product ethylene from the reaction mixture, the equilibrium can be shifted toward the long-chain α,ω-diester and thus the reaction can proceed to completion.



Scheme 1.12: Self-metathesis of methyl undec-10-enoate.[73]

Cross metathesis reactions

In the recent past, especially cross metathesis reactions of readily available plant oils with low molecular weight unfunctionalized olefins have attracted interest. Cross metathesis with ethylene (ethenolysis) splits the fatty acid derivatives at their internal double bonds to terminally unsaturated compounds,[74-84] which are potential platform chemicals for polymers[74,75] and lubricants.[85] In this way for example methyl oleate can be converted with very low amounts of Grubbs first generation catalyst precursor (0.02 mol-% or less) and high conversions to methyl dec-9-enoate and 1-decene (**Scheme 1.13**).[76] The resulting ω-unsaturated fatty acid methyl esters can be further functionalized at their double bonds or dimerized in a self-metathesis reaction, leading to unsaturated long-chain α,ω-diesters (vide supra).[57]



Scheme 1.13: Ethenolysis of methyl oleate.

Starting from methyl oleate or methyl erucate, respectively, in a two-step ethenolysis/self-metathesis process (or directly from methyl undec-10-enoate) a range of long-chain, symmetrically unsaturated α,ω-esters (C_{18}, C_{20} and C_{26}), suitable for polyester synthesis can be prepared.[74,75,86,87] Applying this two-step procedure can be advantageous, particularly on a laboratory scale, even though the longer chain products can be obtained more directly via self-metathesis of the initial fatty acid substrate (cf. **Scheme 1.11**), as product separation and isolation due to the lower molecular weights and boiling points of the intermediate ethenolysis products is facilitated. In practice, ethenolysis reaction conditions comprise a trade-off between selectivity and catalyst productivity in terms of substrate turnover.

Cross metathesis of fatty acid derivatives with short-chain, internally unsaturated olefins can be performed with significantly higher turnovers. For the cross metathesis of methyl oleate with 2-butene, productivities of up to 5 × 10^5 turnovers have been reported.[88,89,90] To achieve this catalytic performance, careful destillative purification of the oleate substrate as well as the utilization of pure, butadiene-free 2-butene is required. Moreover, in this context also a direct butenolysis of triglycerides of different natural occurring plant oils has been reported.

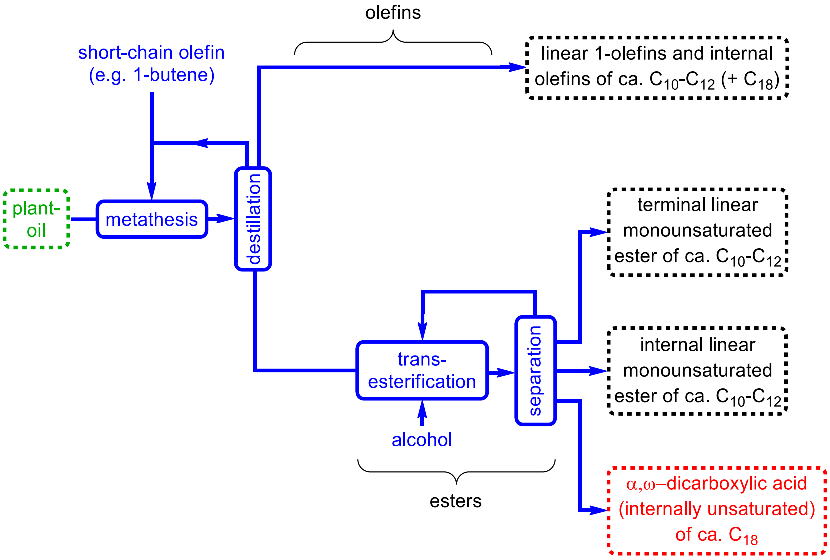


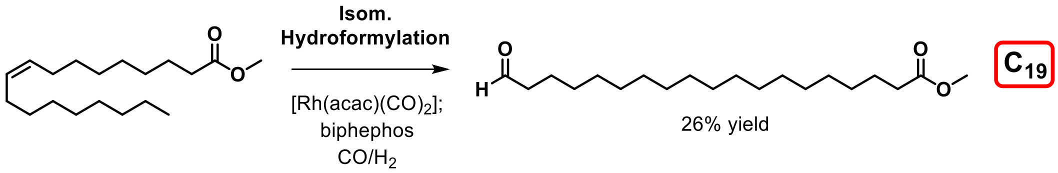
Figure 1.2: Scheme of an alkenolysis process that converts plant oil triglycerides to medium- and long-chain linear olefins and esters.[91]

Butenolysis with 1-butene can be considered a compromise between the desired terminal olefin products and catalyst performance, which also appears to be feasible on a larger scale.[91] A biorefinery by Elevance Renewable Science and Wilmar International in Gresik, Indonesia for the large scale conversion of palm oil by cross metathesis with 1-butene has started operation in 2013.[92-95] Due to the specifics of this process and of olefin metathesis in general, also a significant amount of self-metathesis will occur as a side reaction to yield in particular octadecene-1,18-dioate (**Figure 1.2**). Hydrogenation and hydrolysis of this by-product yields octadecane-1,18-dioic acid, which is marketed currently by Elevance Renewable Science under the trade name Inherent™ C_{18} Diacid in pilot quantitaties.[96]

By contrast to the biotechnological routes discussed (cf. **Chapter 1.3.1**), the preparation of α,ω-difunctional compounds by metathesis chemistry generally utilizes only half of the fatty acid chain. Furthermore, stoichiometric amounts of less valuable byproducts are formed. An alternative chemical catalytic conversion addressing these problems is isomerization functionalization.

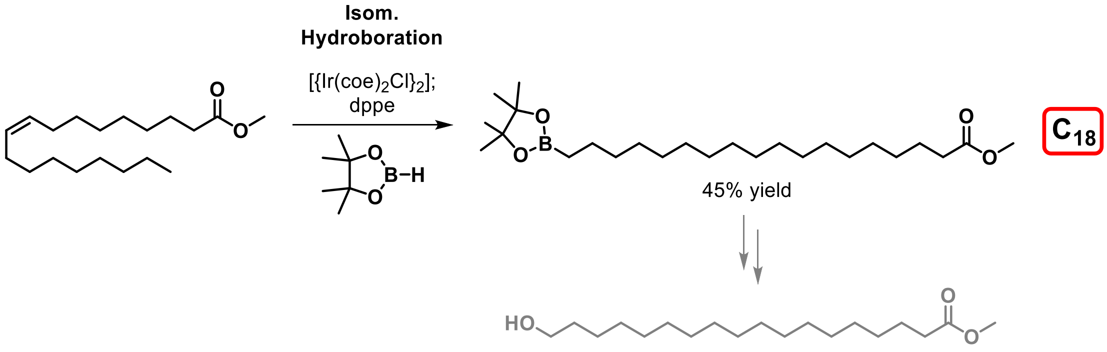
1.3.3 Isomerization functionalization

The aforementioned metathesis reactions construct the α,ω-dicarboxylic acid product from the $=CH(CH_2)_nCOOR$ fragment of the unsaturated fatty acid derivative. The other half of the substrate's chain yields stoichiometric amounts of hydrocarbons. A more efficient use of the plant oil starting materials would be achieved by full incorporation of the hydrocarbon chains into ω-functionalized products. This also gives access to products with other chain lengths (like odd carbon numbered chains), than the aforementioned approaches. This scheme requires an isomerization-functionalization of the carbon-carbon double bond(s) to generate functional groups in the desired terminal positions. Such conversions are challenging to achieve selectively.



Scheme 1.14: Isomerizing hydroformylation of methyl oleate.[97]

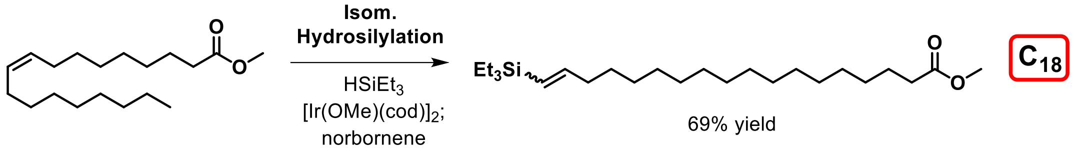
An ω-aldehyde ester was obtained by isomerizing hydroformylation of methyl oleate and methyl linoleate using a rhodium based catalyst system. According to GC/MS yields of 26 % and 34 % were obtained, respectively (**Scheme 1.14**).[97] Competing pathways are the formation of branched aldehydes and double bond hydrogenation of the fatty acid substrate. This was related to the ester group of the substrates, which is considered to favor the hydrogenation pathways via α,β-unsaturated esters formed through isomerization. Consequently, the observed yields are much lower than from analogous reactions of shorter chain alkenes that do not possess an ester functionality such as 4-octene (88 % yield).[98] Nozaki and coworkers recently reported the conversion of internal olefins to terminal alcohols in a tandem isomerization/hydroformylation/hydrogenation reaction applying a rhodium/bisphosphite and the ruthenium based Shvo's catalyst as a combined catalytic system. By reaction of 4-octene a mixture of the terminal alcohol (46 % yield) and the terminal aldehyde (17 % yield) was observed, while for the conversion of methyl oleate to the ω-hydroxy ester an isolated yield of 53 % was obtained.[99]



Scheme 1.15: Isomerizing hydroboration of methyl oleate.[100]

A different approach is provided by trapping of the thermodynamically least-stable terminal double bond isomer from the equilibrium mixture of all double bond isomers in presence of an iridium catalyst with pinacolborane (as the thermodynamically most stable borane in the terminal position, **Scheme 1.15**).[100] The corresponding terminal boronated product was obtained in 45 %

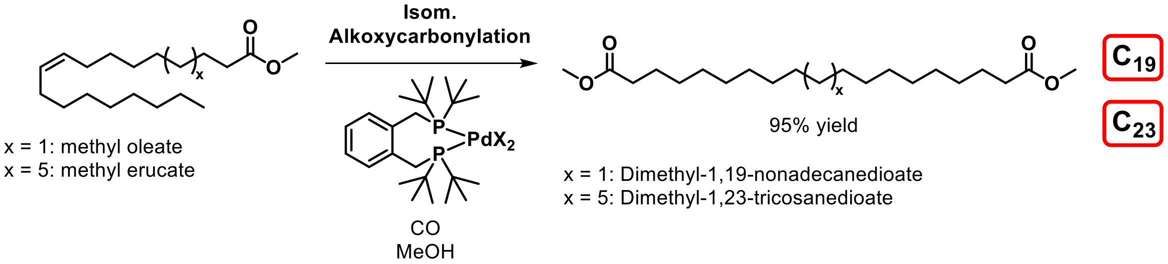
yield (as determined by GC/MS), together with some unidentified isomers and methyl stearate as the hydrogenation by-product (47 % yield). Also in this case, remarkably higher yields of the terminal boronate ester are achieved in the hydroboration of 4-octene.[101] Again the authors suggest, that this might be due to the ester functionality and the formation of the α,β-unsaturated ester isomer, subsequently leading to the hydrogenated product. A significant increase in selectivity in the isomerizing hydroboration of methyl oleate with pinacolborane was reported by Zhu and coworkers applying iridium nanoparticles in the presence of a bulky diphosphane ligand, yielding the desired terminal boronate ester in 78 % isolated yield.[102] After a further oxidation step, terminally borated fatty acids provide a promising access to long-chain ω-hydroxy esters.



Scheme 1.16: Isomerizing dehydrogenative silylation of methyl oleate.[105]

A related approach is given by isomerizing silylation. Early examples of silylation of methyl oleate and other olefins, yielding partially terminal functionalized products, were reported already by Speier *et al.*.[103,104] More recently, Riepl and coworkers reported the selective addition of silane containing groups.[105] Methyl oleate was shown to undergo an iridium catalyzed dehydrogenative silylation with triethylsilane to give the terminal vinylsilane in 69 % yield (**Scheme 1.16**). Besides (isomerized) starting material and some unidentified products only methyl stearate (6 %), i.e. the double bond hydrogenation product, and some internally silylated products (8 %) were obtained. However, transformation of this reaction to other sterically more demanding silanes was not successful, and the unreactive nature of the product's functional groups is not beneficial for further conversions.

Another prominent approach to achieve an isomerizing functionalization is isomerizing alkoxycarbonylation.[106,107] This reaction, first observed for fatty acid esters by Cole-Hamilton and coworkers,[108] converts the internal double bond deep in the hydrocarbon chain very selectively to a terminal ester group by reaction with carbon monoxide and methanol. The reaction is promoted by Pd(II) catalysts with bulky electron-rich diphosphine ligands, like 1,2-bis[(di-*tert*-butylphosphino)methyl]benzene (dtpbx). Dimethyl-1,19-nonadecane dioate and diethyl tricosane-1,23-dioate (via isomerizing ethoxycarbonylation of ethyl erucate) were obtained in in high purity (> 99 % by crystallization from the reaction solvents), enabling utilization for polycondensation reactions.[109] These long-chain α,ω-functionalized diesters can also be obtained in a one-pot procedure from different plant oils,[110] including high oleic sunflower oil.[111] Yields correlate with the oleate content of the starting material, but otherwise the catalyst performance appears not to vary dramatically between pure oleate (99 %) starting material and technical grade methyl oleate (92.5 %) or plant oil (triglyceride). Catalyst performance can be enhanced by utilization of [(dtbpx)Pd(OTf)$_2$] as a defined catalyst precursor, which eliminates the need for using an excess of the diphosphine ligand (**Scheme 1.17**).[112] Utilizing these long-chain α,ω-diesters as platform chemicals, the generation of further monomers, like diols or diamines for the preparation of long-chain polycondensates becomes possible.[109,112]

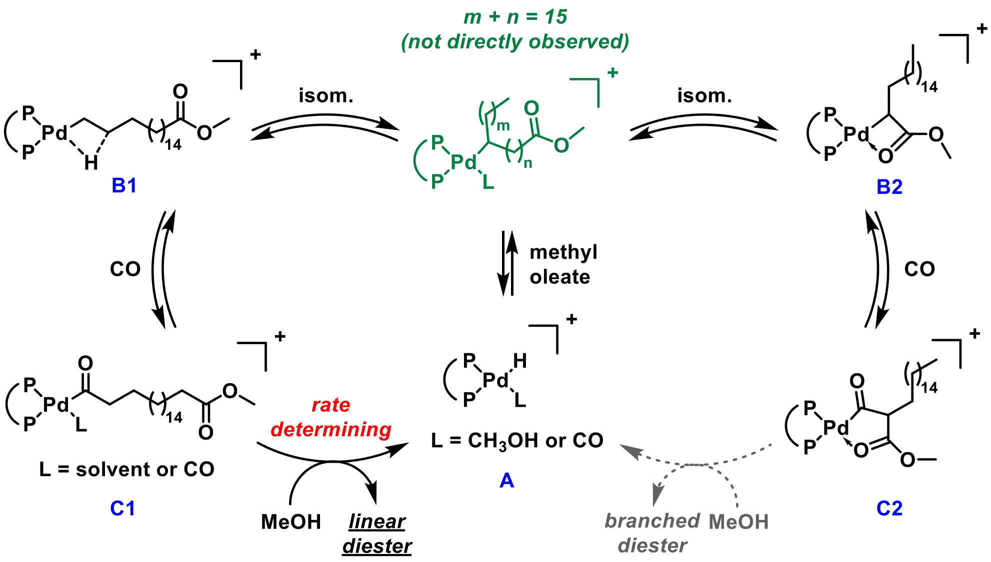


Scheme 1.17: Isomerizing alkoxycarbonylation of methyl oleate and methyl erucate with CO and methanol.[112]

The origin of the remarkable selective transformation within isomerizing alkoxycarbonylation reaction has been unraveled by direct observation of the relevant intermediates via low temperature NMR spectroscopic methods (ca. -80 to -30 °C), supported by DFT calculations (**Scheme 1.18**).[113,114] Starting from the catalytically active hydride species (**A**) the unsaturated fatty acid substrate is isomerized to a linear alkyl species $[(P^\wedge P)PdCH_2(CH_2)_{16}C(=O)OCH_3]^+$ (**B1**) and a branched alkyl (**B2**). Out of the many different branched alkyls conceivable, only this species is formed in observable amounts due to stabilization by coordination of the ester carbonyl group as a four membered chelate $[(P^\wedge P)PdCH\{(CH_2)_{15}CH_3\}C(=O)OCH_3]^+$. In presence of carbon monoxide both intermediates rapidly form the corresponding acyl complexes **C1** and **C2**, respectively. The linear CO insertion product (**C1**) is subject to methanolysis to yield the linear α,ω-diester, which represents the rate-determining step of product formation. By contrast, the resulting branched acyl insertion product (**C2**) resists methanolysis (due to the significantly higher energy barrier compared to methanolysis of the linear acyl species), such that the corresponding branched malonic ester does not form to any significant extent (formation of 0.2 % of malonic ester was revealed from pressure reactor experiments[115]). Nevertheless, the pathway leading to this branched acyl complex (right cycle in **Scheme 1.18**) is not a dead end as all steps are reversible and this dormant species can interconvert within the productive catalytic cycle (left cycle in **Scheme 1.18**). Under pressure reactor conditions (90 °C, 20 bar of CO), all conceivable branched alkyls are formed in very small amounts.

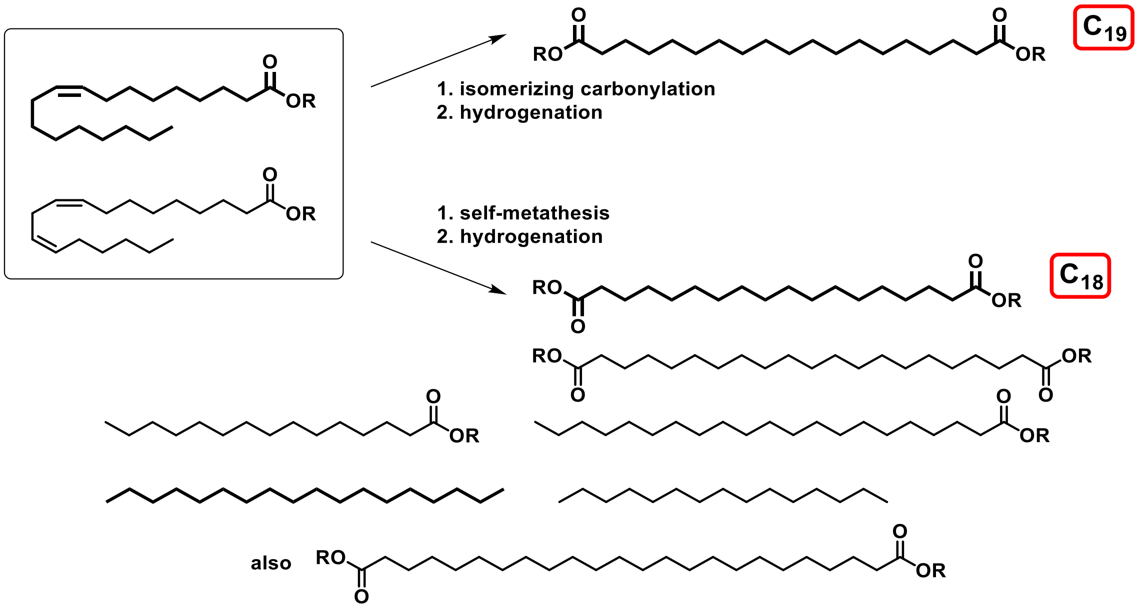
By the utilization of an adamantyl substituted diphosphine ligand, which specifically destabilizes the transition states leading to branched products, an even higher selectivity for the linearα,ω-diester product of 96 % (at 95 % conversion) was achieved.[116]

Scheme 1.18: Major pathways of the isomerizing alkoxycarbonylation of methyl oleate (P^P = $^{t}Bu_2P(CH)_3P^{t}Bu_2$) based on NMR studies[a] (using stoichiometric amounts of methyl oleate and $[(dtbpx)Pd(OTf)_2]$ precursor).[114]



[a] For the methanolysis as the rate determining step ΔG≠ values of 29.1 kcal mol^{-1} for the linear acyl species and 37.7 kcal mol^{-1} for the branched acyl species were calculated from DFT calculations.

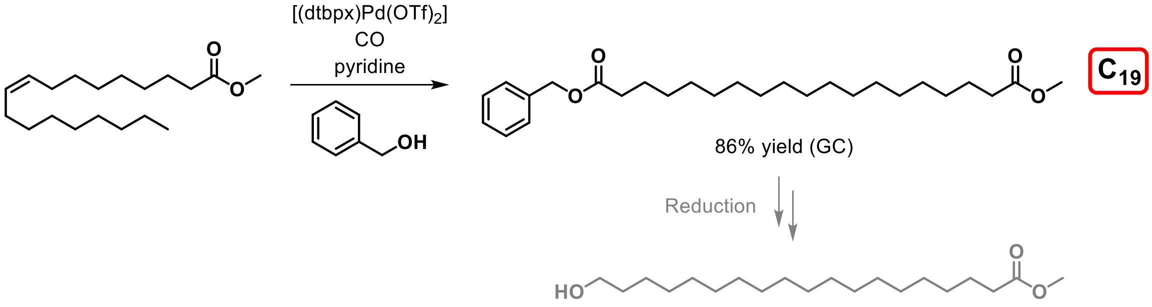
Notably, multiple unsaturated analogues, commonly occurring in monounsaturated fatty acids from natural plant oils, can in principle be converted to the same α,ω-diacid esters (as formed as the main product from the monounsaturated fatty acid starting material) by a sequence of isomerizing carbonylation and catalytic hydrogenation (**Scheme 1.19**).[117]



Scheme 1.19: Major products obtained by isomerizing alkoxycarbonylation (top) and self-metathesis (bottom) of a mixture of an oleate and its double unsaturated analogue linoleate, followed by double bond hydrogenation.

The selectivity in isomerizing methoxycarbonylation of methyl linoleate to the desired unsaturated α,ω-diester is reduced considerably compared to mono-unsaturated substrates. Since the formation of Pd-allyl intermediates increases the energy barrier for the isomerization (and further) steps, the reaction becomes slower.[114] This favors other reaction pathways and, besides the unsaturated α,ω-diester as the main product, amongst others, ketone and methoxy-functionalized monoesters and the (branched) triester are formed.[118] For comparison, a sequence of self-metathesis and subsequent double bond hydrogenation would convert the multiple unsaturated fatty acids to additional α,ω-diacid esters of different chain lengths. This difference between isomerizing carbonylation and olefin metathesis can be related to fundamental characteristics of these reactions: isomerizing carbonylation is strictly kinetically controlled and yields a product not representing the thermodynamically favored outcome. On the other hand, in olefin metathesis often equilibria are obtained as there is no extreme kinetic preference for a particular product.

Isomerizing alkoxycarbonylation is also emerging as a route to unsymmetrical α,ω-difunctionalized products.[119] Considering a preparation of unsymmetric α,ω-diesters, a suppression of transesterification with the alcohol employed as a reactant (and solvent) is crucial. Under appropriate acid-free conditions, transesterification can be suppressed completely (<0.1 %, **Scheme 1.20**). From benzyloxycarbonylation of methyl oleate, the resulting benzyl ester group can be further converted to the corresponding alcohol without affecting the methyl ester group in the same molecule, accessing AB-type monomers for polyester synthesis.

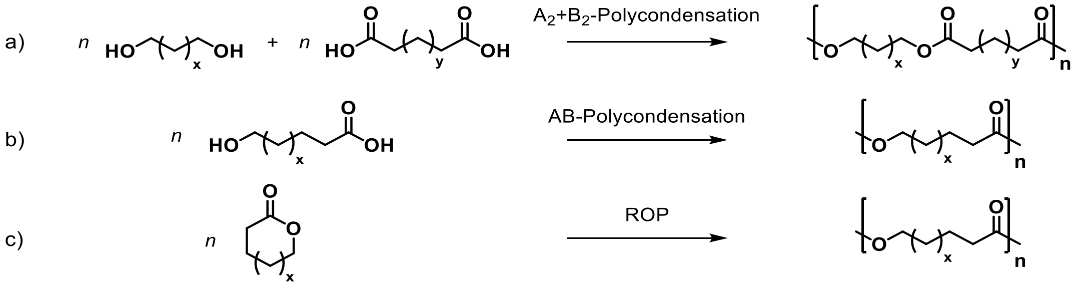


Scheme 1.20: Benzyloxycarbonylation of methyl oleate to yield an unsymmetrical benzyl methyl diester.[119]

1.4 Long-chain aliphatic polyesters

1.4.1 Synthesis of long-chain aliphatic polyesters

Most commonly, polyesters are obtained by direct esterification of dicarboxylic acids and diols in an A_2+B_2 polycondensation with removal of the liberated water (**Scheme 1.21**; a). Alternatively, transesterification (alcoholysis) of diols and diesters can be employed; but also polycondensation of activated monomers such as acid chlorides, acid anhydrides or other carboxylic acid derivatives is well-studied. In contrast to the direct esterification, transesterification proceeds very slowly, even at high reaction temperatures. Thus, for the preparation of high molecular weight polyesters the presence of a catalyst is generally required. A large range of catalysts has been reported. Metal salts and oxides such as zinc acetate and diantimony trioxide, as well as organometallic compounds, mainly titanium and zirconium alkoxides, have been found to be active.[120,121]



Scheme 1.21: Polyester synthesis from (a) polycondensation of a diacid (or derivative) and a diol, (b) polycondensation of an ω-hydroxy acid and (c) ring opening polymerization of a lactone.

Despite their large scale applications, achieving a desirably high molecular weight for a novel polycondensation system under study is an issue and no generic protocols exist, that can be transferred to a novel combination of monomers of interest. According to the relationship between the degree of polymerization (DP_n) and the functional group conversion described by Carothers, very high conversions are necessary to obtain polycondensates of sufficiently high molecular weights (typically on the order of several 10^4 g mol^{-1}) for individual applications.[122,123] In order to achieve any substantial molecular weight, often high temperatures, long reaction times and an efficient removal of undesired by-products are required. Poly(ethylene terephthalate) (PET, T_m = 268 °C) for example, the largest volume commercial polyester, is prepared by direct polyesterification of purified terephthalic acid with an excess of ethylene glycol under reduced pressure at elevated temperatures up to 290 °C.[121] In the course of polycondensation the excess of glycol is removed and high degrees of polymerization ($DP_n \approx 200$) are obtained.

In polycondensation reactions of long-chain aliphatic dicarboxylic acids such an excess of the diol component can also be applied, if the short-chain diols used are volatile under polycondensation conditions. However, this does not apply when long-chain diols are employed,[109,112,124] as their high boiling points hinder the removal of the excess to reach sufficiently high molecular weights (e.g. for tetradecane-1,14-diol boiling point is > 200 °C at 9 Torr[26]). Thus, already in the initial reaction mixture, an accurate stoichiometric balance between the diol and the diacid (or the diacid derivative) is required. This obviously does not apply to an AB-type approach, applying ω-hydroxy acids (**Scheme 1.21**; b)[125] However, such unsymmetric monomers are less well accessible in general.

An alternative route to long-chain aliphatic polyesters is ring-opening polymerization (ROP) of cyclic monomers (**Scheme 1.21**; c). As a chain-growth reaction ROP is not subjected to the aforementioned restrictions of step-growth polycondensations. However, besides ω-pentadecalactone, which can be directly derived from *Angelica archangelica L.* root oil,[126] large ring lactones in general are less readily available than e.g. long-chain dicarboxylic acids.

1.4.2 Typical properties of long-chain aliphatic polyesters

Today's applications of polyesters are dominated by materials based on aromatic diacids, most prominently polycondensates of terephthalic acid with C_2 to C_4 linear diols. Applications of entirely aliphatic polyesters in contrast are limited to smaller scale specialties. One reason is certainly given by their low melting points, making thermoplastic processing problematic due to low crystallization temperatures (apart from very short-chain aliphatic polyesters like polylactic acid or polybutylene succinate).[127,128,129] Also an undesired softening in applications e.g. at elevated ambient temperature could be problematic (e.g. poly(ε-caprolactone) melts at T_m of ca. 60 °C and poly(butylenes adipate) at T_m of ca. 55 °C, cf. **Table 1.2**). This lower crystallinity also goes along with a decreasing stability toward hydrolytic degradation which may be undesirable for a given application. These potential drawbacks of short and mid-chain all-aliphatic polyesters can, however, be overcome by introduction of longer, crystallizable methylene segments.

Table 1.2: Melting points of different all-aliphatic linear polyesters of the **PE-X.Y** type.

	Number of carbon atoms in the diol, X																					
Number of carbon atoms in the diacid component, Y	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**	**21**	**22**	**23**
2	160[143]	66[141]	105[137] 103[141]	49[141]	70[137] 71[143]		75[137]		78[137] 76[143]		91[137]				95[137]				88[141]			
3	-20[143] liq.[144]	-25[141]	-24[141]	-26[141]	-48[143]				29[143]										67[141]			
4	102[143] 108[144]	43[141] 52[144]	113[141]	32[141]	52[143] 57[144]				71[143] 68[144]		73[10]								86[141]		92[10]	
5	-16[143]	35[141]	36[141]	22[141]	28[141]				55[143]		67[10]								77[141]		87[10]	
6	49[143] 50[144]	36[141] 45[144]	55[141]	37[141]	55[143] 56[144]	38-45[136]	67[133] 72[134]		70[143] 77[144]		75[10] 78[133]		80[133]		86[133]				85[141]		93[10]	
7	27[143]	41[141]	38[141]	39[141]	52[143]		61[135]		63[143]		77[139]								82[141]			
8	64[143]	47[141]	61[138]	43[141]	61[143]		70[133] 69[135]		70[143]		79[10] 80[133]		82[133]		87[133]				86[141]		92[10]	
9	45[143]	46[141] 51[142]	49[141]	46[141] 49[142]	52[143]		65[135]		67[143]		34-63[136]								84[141]			
10	73[143] 79[144]	49[141] 56[144]	54[141] 63[138]	53[141]	65[143] 67[144]		72[135]		71[143] 74[144]		82[131]								87[141]			
11		67[142]		58[142]																		
12	85[145]	67[145]	77[145] 72[138]		77[145]		76[145]		83[139] 83[145]		84[139] 88[145]											
13		75[142]		64[142]																		
14			76[139]								89[139]				94[139]							
15																						
16	92[146]				80[146]																	
17																						
18	95[146]		84[146]		82[146]		88[50]		93[132]													
19					86[109]						93[112]							103[109]				
20																			108[73]			
21																						
22																						
23			85[140]		92[112] 92[140]						101[112] 101[140]							106[112]				108[109]

Other long-chain aliphatic polyesters: **PE-30.30**: 113 °C;[124] **PE-38.23**: 109 °C and **PE-44.23**: 111 °C;[130] **PE-44.5**: 102 °C.[10]

Although general trends such as the increase of the melting point with increasing hydrocarbon chain length of the diol or the diacid component become evident, gaps in the data, especially for long-chain monomers, and the great variation that is often found between the values given by different authors complicate the derivation of a comprehensive picture. Korshak *et al.* prepared a number of aliphatic polyesters based on eicosane-1,20-diol.[147] They clearly demonstrated, that the melting points of the polyesters obtained not only depend on the number of carbon atoms in the diacid monomer, but also on whether this number is even or odd (**Figure 1.3**).

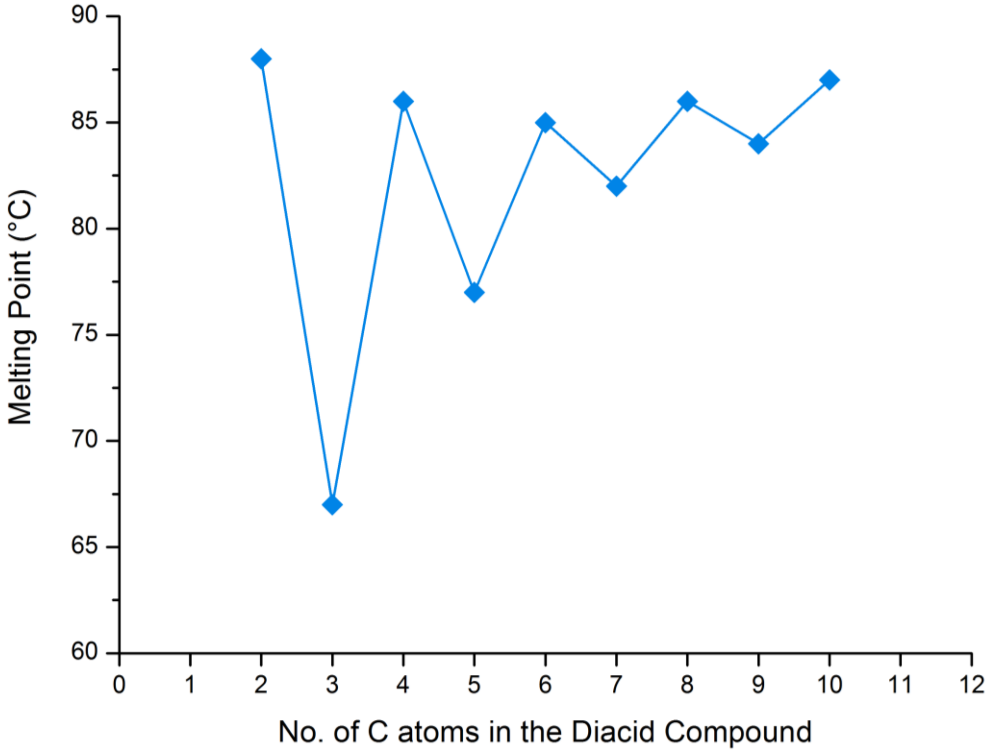


Figure 1.3: Melting points of polyesters-20.X with α,ω-diacid repeat units of different chain lengths.[147]

In general, polyesters derived from dicarboxylic acids containing even numbers of carbon atoms melt at higher temperatures than those derived from diacids containing odd numbers of carbon atoms. This observation was ascribed to the fact, that the crystalline phase of an aliphatic polyester with an even number of carbon atoms between ester groups contains close layers of dipoles of opposite direction (effectively canceling the local polarization), whereas close carbonyl layers of identical direction are present in the crystal of polyesters derived from dicarboxylic acids having odd numbers of carbon atoms (**Figure 1.4**).[148,149,150]

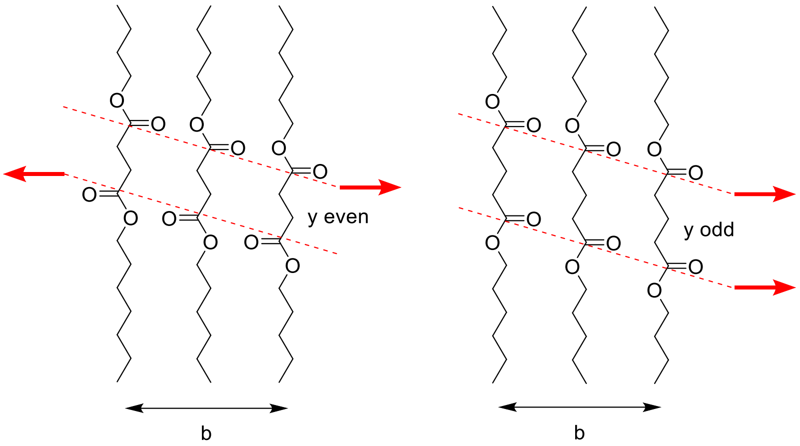


Figure 1.4: Schematic illustration of the arrangement of the polar layers in aliphatic polyesters with even number of carbons between the ester groups (left) and odd number of carbons between ester groups (right), to account for the observed trends in the melting behavior. The arrows indicate the directions of polarizations.[128]

Parallel to the odd-even effect in the melting behavior, also variations in the crystalline structures are observed for these polyesters. While an orthorhombic unit cell is generally found for polyesters with odd numbers of carbon atoms in the (short-chain) diacid repeat unit, monoclinic structures are found for even-numbered congeners. Obviously, for these latter polyesters distorted chain conformations (compared to the all-*trans* orthorhombic structure) increase the overall crystalline stability.[151]

With increasing numbers of methylene groups in the dicarboxylic acid the extent of this odd-even effect decreases and the orthorhombic crystal structure becomes dominant for all long-chain polyesters (vide infra). However, the melting point of an aliphatic polyester depends not only on the total number of methylene groups in a link, but also on their distribution within the polymer chain (e.g. T_m(**PE-6.8**) = 65 - 68 °C; T_m(**PE-10.4**) = 70 - 74 °C).[128]

In general, the solid-state structures of long-chain aliphatic polyesters are dominated by *van-der-Waals* interactions between adjacent stretched methylene sequences, that is, by their hydrocarbon nature. For linear, long-chain A_2+B_2-polyesters (where both diacid and diol monomer compounds have long-chain character) generally orthorhombic, polyethylene-like crystal structures are found (**Figure 1.5**),[109,112,152,153,154] since the ester groups (acting as structural defects along the crystalline polymer chains) have no fundamental influence on the crystallization of hydrocarbon segments in the all-*trans* zigzag conformation. Typically, narrow melting transitions and distinct melting points, together with crystallinities up to 80 % are observed (compared to fully extended chain crystals of linear polyethylene as a reference for 100 % crystalline material).[109,112]

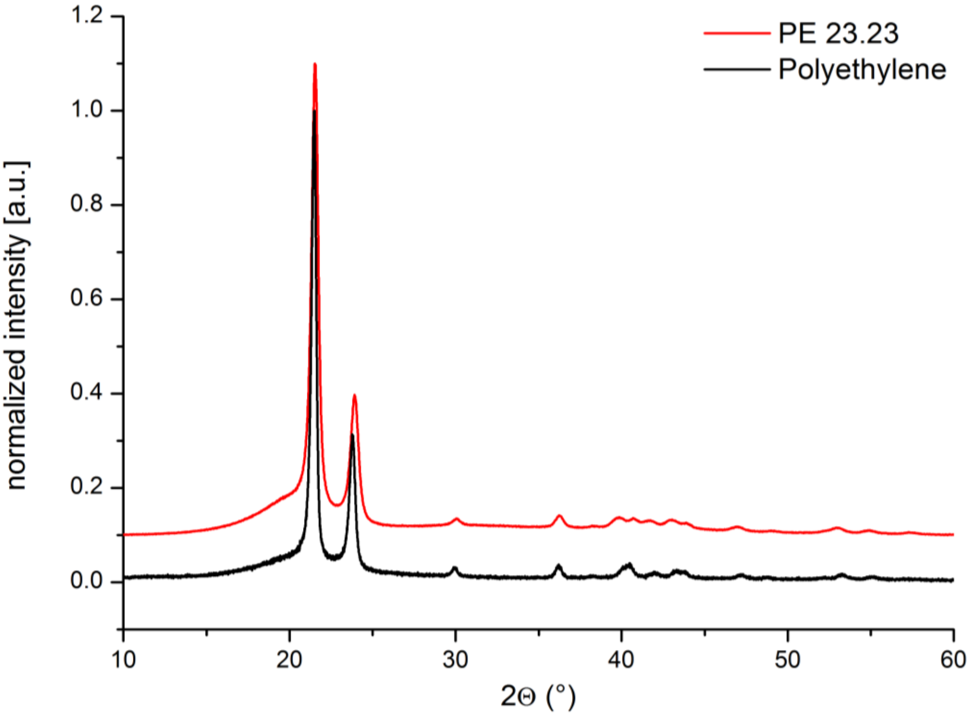


Figure 1.5: Wide-angle X-ray diffraction (WAXD) patterns of **PE-23.23** poly[1,23-tricosadiyl-1,23-tricosanedioate] (red) and linear polyethylene (black).

Consequently, these novel materials are frequently discussed as “polyethylene mimics” or “polyethylene-like”.[145,155,156,157] By means of solid-state NMR and SAXS data, Schmidt-Rohr and coworkers elucidated the solid state structure of **PE-22.4** in detail (**Figure 1.6**).[158]

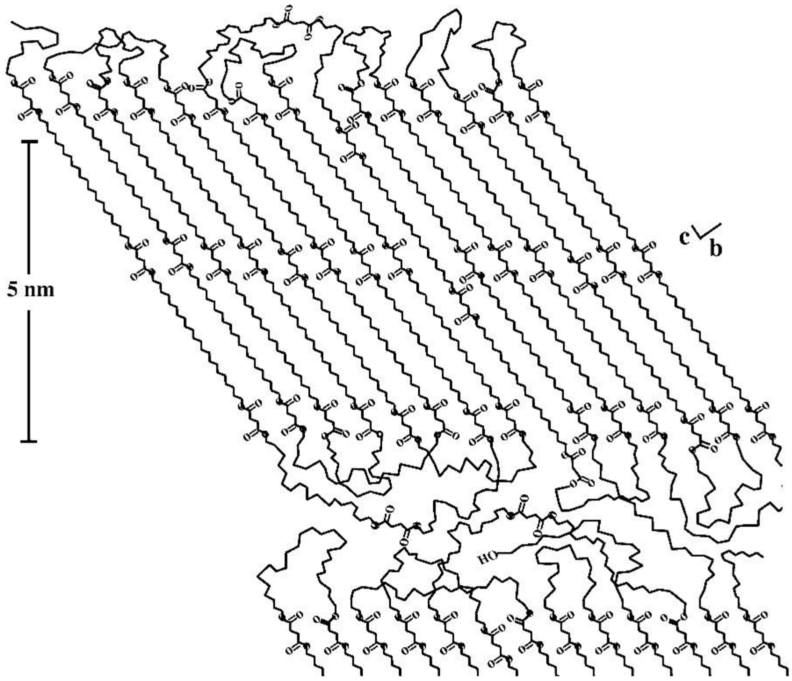
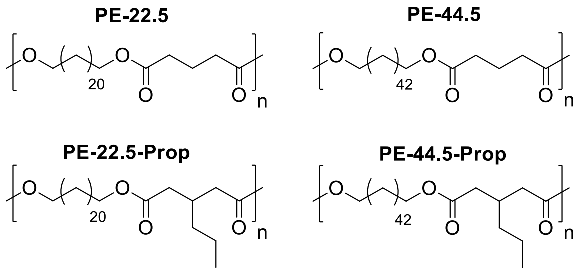


Figure 1.6: Solid state structure of the aliphatic polyester **PE-22.4** according to detailed NMR and SAXS studies.[158]

Their results show, that the ester functionalities exert a detectable influence on the crystalline chain arrangements as well as the crystal thickness (while still allowing for crystallization in a polyethylene-like crystal structure). In **PE-22.4** typically three diester layers can be found in the crystal; two of them at the surface and one in the center (**Figure 1.6**). Related observations were made for **PE-22.5** and **PE-44.5**.[10,154] In contrast to their branched analogues **PE-22.5-Prop** and **PE-44.5-Prop** (**Scheme 1.22**), which reject the propyl side chains outside the crystalline phase, these two linear examples also feature an inclusion of polar ester groups into the crystal lattice. Also for AB-type polyesters like ROP-generated poly(pentadecalactone) (and its copolymers with ε-caprolacton) the orthorhombic unit cell with dimensions comparable to polyethylene is observed.[159,160]



Scheme 1.22: Chemical structures of the polyesters investigated by Le Fevere de Ten Hove *et al.*[154]

Dynamic mechanical analysis (DMA) on poly(pentadecalactone) with a number average molecular weight of 6.5×10^{4} g $\mathrm{mol^{-1}}$ (determined by GPC vs. polystyrene standards) revealed a glass transition at -27 °C and a high storage modulus, attributed to high crystallinity as determined by DSC (64 %, compared to linear polyethylene) and WAXD (54 %).[161] Mechanical analyses on poly(pentadecalactone) samples with different molecular weights exhibit a strong dependence of the mechanical properties on the molecular weight in the regime studied (**Table 1.3**).[162]

Table 1.3: Young's modulus, stress at yielding, strain at yielding, stress at break and elongation at break, for poly(pentadecalactone) samples of different molecular weights.[162]

entry	M_w[a] [g $\mathrm{mol^{-1}}$]	Young's modulus [MPa]	Stress at yield [MPa]	Strain at yield [%]	Stress at break [MPa]	Elongation at break [%]
1	4.5×10^4	690 ± 40			20.4 ± 3.2 (21.3 ± 3.3)[b]	4.5 ± 0.8
2	8.1×10^4	620 ± 50	24.1 ± 2.0	12.0 ± 1.0	17.7 ± 1.3 (42.0 ± 3.0)[b]	137 ± 25
3	18.9×10^4	450 ± 20	17.2 ± 0.3	13.0 ± 1.0	16.2 ± 0.5 (60.8 ± 2.0)[b]	650 ± 28
4	28.0×10^4	290 ± 30	13.3 ± 1.3	20.6 ± 1.3	13.7 ± 1.0 (55.0 ± 4.0)[b]	703 ± 72
5	48.1×10^4	390 ± 10	18.2 ± 0.3	17.4 ± 0.4	17.3 ± 0.9 (58.8 ± 3.1)[b]	580 ± 30

a) Determined by GPC in chloroform against polystyrene standards. b)True stress at break calculated after cross-section area correction.

Gross and coworkers observed a brittle to ductile transformation for low molecular weight samples with M_w values between 4.5×10^4 g mol^{-1} and 8.1×10^4 g mol^{-1} (**Table 1.3**; entry 1 and 2). Moreover, with elongations at break and stresses at break reaching asymptotic values of 650 % and 16 MPa, respectively, these high molecular weight samples also exhibit mechanical properties comparable to those of high density polyethylene. Similar trends were observed for poly(ω-hydroxytetradecanoate) with its slightly shorter C_{14} repeat units.[125]

Concerning the mechanical properties of linear long-chain A_2+B_2 type polyesters, Cho and Lee investigated **PE-30.30**.[124] However, an elongation of break of only 5 % was found, indicating that the molecular weight of the material was likely insufficient. Yet, besides these data, further investigations on the mechanical properties of entirely long-chain A_2+B_2 type polyesters have not been reported so far.

1.5 References

1. Carothers, W. H. in *Collected Papers of Wallace Hume Carothers on High Polymeric Substances*, Mark, H.; Whitby, G. S., Eds.; Interscience Publishers: New York, **1940**.
2. Polyurethanes from Vegetable Oils. Petrović, Z. S. *Polym. Rev.* **2008**, *48*, 109-155.
3. Oleochemical Products as Building Blocks for Polymers. Heidbreder, A.; Höfer, R.; Grützmacher, R.; Westfechtel, A.; Blewett, C. W. *Fett/Lipid* **1999**, *101*, 418-424.
4. Fats and Oils as Oleochemical Raw Materials. Hill, K. *Pure Appl. Chem.* **2000**, *72*, 1255-1264.
5. Chemical Routes for the Transformation of Biomass into Chemicals. Corma, A.; Iborra, S.; Velty, A. *Chem. Rev.* **2007**, *107*, 2411-2502.
6. Biopolyester Membranes of Plants: Cutin and Suberin. Kolattukudy, P. E. *Science* **1980**, *208*, 990-1000.
7. Silvestre, A. J. D.; Neto, C. P.; Gandini, A., Chapter 14 - Cork and Suberins: Major Sources, Properties and Applications. In *Monomers, Polymers and Composites from Renewable Resources*, Gandini, M. N. B., Ed.; Elsevier: Amsterdam, **2008**; 305-320.
8. Synthesis of 1,44-Tetratetracontanediol. Rusanova, E. E.; Sebyakin, Y. L.; Volkova, L. V.;. Evstigneeva, R. P. *J. Org. Chem. USSR* **1984**, *20*, 248-251.
9. From Aliphatic Polyesters to “Contaminated” Polyethylenes: Synthesis and Solid-State Characterization of Potentially Self-Organizing Polyesters. Penelle, J.; Le Fevere de Ten Hove, C.; Schall, J.; Jonas, A.; Hu, W.; Schmidt-Rohr, K.; Waddon, A. J. *Polym. Prepr.* **1999**, *40*, 617-618.
10. Controlling Solid-State Microstructure of Semi-Crystalline Polymers through Chemical Design of Chains: a Study of Model Polyesters. Le Fevere de Ten Hove, C. PhD thesis, Université catholique de Louvain, Louvain-la-Neuve (**2001**).
11. Studies on the Synthesis of Linear Aliphatic Compounds. Part. 3 The Synthesis of Paraffins with Very Long Chains. Bidd, I.; Holdup, D. W.; Whiting, M. C. *J. Chem. Soc., Perkin Trans. 1* **1987**, 2455-2463.
12. A versatile Process for the Syntheses of Very Long-Chain Alkanes, Functionalised Derivatives and some Branched Chain Hydrocarbons. Brooke, G. M.; Burnett, S.; Mohammed, S.; Proctor, D.; Whiting, M. C. *J. Chem. Soc., Perkin Trans. 1* **1996**, 1635-1645.
13. Schäfer, H.-J., Recent contributions of Kolbe electrolysis to organic synthesis. In *Electrochemistry IV*, Steckhan, E., Ed.; Springer: Berlin Heidelberg: **1990**; *Vol. 152*, 91-151.
14. Elektrolytische Synthese zweibasischer Säuren. Brown, A. C.; Walker, J. *J. Liebigs Ann. Chem.* **1891**, *261*, 107-128.

15. The Electrosynthesis of N-Duotricontanedicarboxylic Acid. Fairweather, D. A. *Proc. R. Soc. Edinburgh* **1925**, *45*, 283-285.
16. Electrosynthesis in the Series of Normal Dibasic Acids. Fairweather, D. A. *Proc. R. Soc. Edinburgh* **1926**, *46*, 71-75.
17. Electroorganic Synthesis 65. Anodic Homocoupling of Carboxylic Acids Derived from Fatty Acids. Weiper-Idelmann, A.; aus dem Kahmen, M.; Schaefer, H. J.; Gockeln, M. *Acta Chem. Scand.* **1998**, *52*, 672-682.
18. The Synthesis of Higher Aliphatic α,ω-Dicarboxylic Acids. Kreuchunas, A. *J. Am. Chem. Soc.* **1953**, *75*, 3339-3344.
19. Synthesis of Fatty Acids Using Organocopper (I) Ate Complexes Derived from Grignard Reagents. Bergbreiter, D. E.; Whitesides, G. M. *J. Org. Chem.* **1975**, *40*, 779-782.
20. Docosanedioic Acid. Hünig, S.; Lücke, E.; Brenninger, W. *Organic Syntheses*, Coll. Vol. 5, p.533 (**1973**); Vol. 43, p.34 (**1963**).
21. Synthesen mit Enaminen, III. Kettenverlängerung von Dicarbonsäuren um 6 und 12 C-Atome. Hünig, S.; Lücke, E. *Chem. Ber.* **1959**, *92*, 652-662.
22. Synthesen mit Enaminen, V. Kettenverlängerung von Mono- und Dicarbonsäuren um 5 bzw. 10 C-Atome. Hünig, S.; Lendle, W. *Chem. Ber.* **1960**, *93*, 913-920.
23. Synthesen mit Enaminen, XVI. Kettenverlängerung von Mono- und Dicarbonsäuren um 12 C-Atome. Hünig, S.; Buysch, H.-J. *Chem. Ber.* **1967**, *100*, 4010-4016.
24. Synthesen mit Enaminen, XVII. Kettenverlängerung von Dicarbonsäuren um 24 C-Atome. Hünig, S.; Buysch, H.-J. *Chem. Ber.* **1967**, *100*, 4017-4026.
25. Synthèse de l'Acide Heptacontane-Dioïque Normal. Wakselman, M. C. *C. R. Hebd. Seances Acad. Sci.* **1964**, *260*, 5056-5058.
26. Préparation d'Acides Polyméthylène-Dicarboniques de 11 à 19 Atomes de Carbone et de quelques-uns de Leurs Dérivés. Chuit, P. *Helv. Chim. Acta* **1926**, *9*, 264-278.
27. Réduction des Ethers Diméthyliques des Acides Polyméthylène-Dicarboniques de 15 à 21 Atomes de Carbone, par le Sodium et l'Alcool. Chuit, P.; Hausser, J. *Helv. Chim. Acta* **1929**, *12*, 850-859.
28. Über vielgliedrige Ringsysteme: VI. Die Bildungstendenz von Polymethylenketonen mit mehr als 20 Kohlenstoffatomen. Ziegler, K.; Hechelhammer, W. *J. Liebigs Ann. Chem.* **1937**, *528*, 114-142.
29. Zur Darstellung langkettiger Carbonsäuren durch hydrolytische Spaltung carbocyclischer Verbindungen. Lettré, H.; Jahn, A. *Chem. Ber.* **1952**, *85*, 346-351.

30. Synthesis of Odd-Numbered Keto Dibasic Acids and Corresponding Saturated Acids. Blomquist, A. T.; Johnson, J. R.; Diuguid, L. I.; Shillington, J. K.; Spencer, R. D. *J. Am. Chem. Soc.* **1952**, *74*, 4203-4204.
31. Über einige höhere normale α,ω-Dicarbonsäuren. Günthard, H. H.; Heinemann, S. D.; Prelog, V. *Helv. Chim. Acta* **1953**, *36*, 1147-1159.
32. Über die Darstellung langkettiger Carbonsäuren unter Verwendung von Vinyl-[ω-alkoxycarbonyl-alkyl]-ketonen, VII. Triacontan-dicarbonsäure-(1.30) und Nonatriacontan-dicarbonsäure-(1.39). Buchta, E.; Huhn, C. *J. Liebigs Ann. Chem.* **1966**, *695*, 42-48.
33. Synthese langkettiger, endständig bifunktioneller Alkan- und Alkin-Derivate. Schill, G.; Merkel, C. *Chem. Ber.* **1978**, *111*, 1446-1452.
34. One-Step Synthesis of Long-Chain Aliphatic α,ω-Dicarboxylic Acids Utilizing the Copper-Catalyzed Reaction of β-Propiolactone with α,ω-Di-Grignard Reagents. Fujisawa, T.; Sato, T.; Kawara, T.; Tago, H. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 345-346.
35. Synthesis of α,ω-Alkanediols. A review. Patwardhan, S. A. *Org. Prep. Proced. Int.* **1994,** *26*, 645-670.
36. Rilsan (Polyamid 11), Synthese und Eigenschaften. Genas, M. *Angew. Chem.* **1962**, *74*, 535-540.
37. Production, Chemistry, and Commercial Applications of Various Chemicals from Castor Oil. Naughton, F. C. *J. Am. Oil Chem. Soc.* **1974**, *51*, 65-71.
38. Brehmer, B., Polyamides from Biomass Derived Monomers. In *Bio-Based Plastics: Materials and Applications*, Kabasci, S., Ed.; Wiley: Chichester, **2004**, 275-294.
39. Method of Making Azelaic Acid. Goebel, C. G.; Brown, A. C.; Oehlschlaeger, H. F.; Rolfes, R. P. (Emery Industries), U.S. Patent 2,813,113 A (**1957**).
40. Verhé, R. G., Industrial Products from Lipids and Proteins. In *Renewable Bioresources: Scope and Modification for Non-Food Applications*, Stevens, C. V.; Verhé, R. G., Eds.; Wiley: Chichester: **2004**, 208-250.
41. Fermentative Herstellung der α,ω-Dicarbonsäure 1,18-Oktadecendisäure als Grundbaustein für biobasierte Kunststoffe. Zibek, S.; Huf, S.; Wagner, W.; Hirth, T.; Rupp, S. *Chem. Ing. Tech.* **2009**, *81*, 1797-1808.
42. Lipid Biotechnology: Industrially Relevant Production Processes. Schörken, U.; Kempers, P. *Eur. J. Lipid Sci. Technol.* **2009**, *111*, 627-645.
43. Biotechnological Synthesis of Long-Chain Dicarboxylic Acids as Building Blocks for Polymers. Huf, S.; Krügener, S.; Hirth, T.; Rupp, S.; Zibek, S. *Eur. J. Lipid Sci. Technol.* **2011**, *113*, 548-561.

44. Weiss, A. Selective Microbial Oxidations in Industry. In *Modern Biooxidation;* Schmid, R. D.; Urlacher, V. L., Eds.; Wiley-VCH: Weinheim, **2007**; 193-210.
45. Determination of Candida tropicalis Acyl Coenzyme A Oxidase Isozyme Function by Sequential Gene Disruption. Picataggio, S.; Deanda, K.; Mielenz, J. *Mol. Cell. Biol.* **1991**, *11*, 4333-4339.
46. Transformation of Fatty Acids Catalyzed by Cytochrome P450 Monooxygenase Enzymes of Candida tropicalis. Eschenfeldt, W. H.; Zhang, Y.; Samaha, H.; Stols, L.; Eirich, L. D.; Wilson, C. R.; Donnelly, M. I. *Appl. Environ. Microbiol.* **2003**, *69*, 5992-5999.
47. Engineering the acetyl-CoA Transportation System of Candida tropicalis Enhances the Production of Dicarboxylic acid. Cao, Z.; Gao, H.; Liu, M.; Jiao, P. *Biotechnol. J.* **2006**, *1*, 68-74.
48. Metabolic Engineering of *Candida Tropicalis* for the Production of Long-Chain Dicarboxylic Acids. Picataggio, S.; Rohrer, T.; Deanda, K.; Lanning, D.; Reynolds, R.; Mielenz, J.; Eirich, L. D. *Nat. Biotech.* **1992**, *10*, 894-898.
49. Site-specific Modification of the Candida Tropicalis Genome. Picataggio, S., Deanda, K., Eirich, L. D. (Henkel Research Corp.) WO 1991/06660 (**1991**).
50. Two-Step Biocatalytic Route to Biobased Functional Polyesters from ω-Carboxy Fatty Acids and Diols. Yang, Y.; Lu, W.; Zhang, X.; Xie, W.; Cai, M.; Gross, R. A. *Biomacromolecules* **2010**, *11*, 259-268.
51. Biosynthesis of Monomers for Plastics from Renewable Oils. Lu, W.; Ness, J. E.; Xie, W.; Zhang, X.; Minshull, J.; Gross, R. A. *J. Am. Chem. Soc.* **2010**, *132*, 15451-15455.
52. Biosynthetic Routes to Long-Chain α,ω-Hydroxyacids, Diacids and their Conversion to Oligomers and Polymers. Gross, R. A., Lu, W., Ness, J., Minshull, J. (Polytechnic Institute of New York University), WO 2011/008232 (**2011**).
53. Downstream Processing Research for Biotechnological Production on 1,18 Octadecene Acid. Körner, H. J.; Deerberg, G. *Chem. Ing. Tech.* **2009**, *81*, 1823-1828.
54. In Germany risk group classification is used to rate pathogenicity of microorganisms; cf. Biostoffverordnung: Verordnung über Sicherheit und Gesundheitsschutz bei Tätigkeiten mit biologischen Arbeitsstoffen (BioStoffV) 27th January, 1999 (BGBl. I S. 50), last changed by Art. 3V on 12/18/2008.
55. Mikrobiologische Herstellung von Industriechemikalien. Grundlagen der Dicarbonsäure-bildung mit Hefen. Schindler, J.; Meussdoerffer, F.; Giesel-Bühler, H. *Forum Mikrobiologie* **1990**, *13*, 274-281.
56. Industrial Biotechnology Provides Opportunities for Commercial Production of new Long-Chain Dibasic Acids. Kroha, K. *Inform.* **2004**, *15*, 568-571.

57. Metathese ungesättigter Fettsäureester - ein einfacher Zugang zu langkettigen Dicarbonsäuren. Warwel, S.; Jägers, H. G.; Thomas, S. *Lipid/Fett* **1992**, *94*, 323-328.
58. Application of Olefin Metathesis in Oleochemistry: an Example of Green Chemistry. Mol, J. C. *Green Chem.* **2002**, *4*, 5-13.
59. Metathesis of Unsaturated Fatty Acid Esters and Fatty Oils. Mol. J. C. *J. Mol. Catal.* **1994**, *90*, 185-199.
60. Catalytic Metathesis of Unsaturated Fatty Acid Esters and Oils. Mol. J. C. *Top. Catal.* **2004**, *27*, 97-104.
61. Metathesis as a Versatile Tool in Oleochemistry. Rybak, A.; Fokou, P. A.; Meier, M. A. R. *Eur. J. Lipid Sci. Technol.* **2008**, *110*, 797-804.
62. Metathesis with Oleochemicals: New Approaches for the Utilization of Plant Oils as Renewable Resources in Polymer Science. Meier, M. A. R. *Macromol. Chem. Phys.* **2009**, *210*, 1073-1079.
63. a) Catalysis at the Interface of Ruthenium Carbene and Ruthenium Hydride Chemistry: Organometallic Aspects and Applications to Organic Synthesis. Schmidt, B. *Eur. J. Org. Chem.* **2004**, *2004* (9), 1865-1880. b) Olefin Metathesis and Isomerization: From Undesired Side Reactions to Useful Synthetic Methodology. Schmidt, B. *J. Mol. Catal. A: Chem.* **2006**, *254*, 53-57.
64. Metathesis of Unsaturated Fatty Acid Esters by a Homogeneous Tungsten Hexachloride-tetramethyltin Catalyst. Van Dam, P. B.; Mittelmeijer, M. C.; Boelhouwer, C. *J. Chem. Soc., Chem. Commun.* **1972**, *22*, 1221-1222.
65. Homogeneous Catalytic Metathesis of Unsaturated Fatty Esters: New Synthetic Method for Preparation of Unsaturated Mono- and Dicarboxylic Acids. Van Dam, P.; Mittelmeijer, M.; Boelhouwer, C. *J. Am. Oil Chem. Soc.* **1974**, *51*, 389-392.
66. Heterogeneous Metathesis of Unsaturated Fatty Acid Esters. Verkuijlen, E.; Kapteijn, F.; Mol, J. C.; Boelhouwer, C. *J. Chem. Soc., Chem. Commun.* **1977**, *7*, 198-199.
67. The Development of L_2X_2RuCHR Olefin Metathesis Catalysts: An Organometallic Success Story. Trnka, T. M.; Grubbs, R. H. *Acc. Chem. Res.* **2000**, *34*, 18-29.
68. Ruthenium-Based Heterocyclic Carbene-Coordinated Olefin Metathesis Catalysts. Vougioukalakis, G. C.; Grubbs, R. H. *Chem. Rev.* **2010**, *110*, 1746-1787.
69. High Turnover Numbers with Ruthenium-Based Metathesis Catalysts. Dinger, M. B.; Mol, J. C. *Adv. Synth. Catal.* **2002**, *344*, 671-677.
70. Metathesis of Unsaturated Fatty Acids: Synthesis of Long-Chain Unsaturated α,ω-Dicarboxylic Acids, Ngo, H. L.; Jones, K.; Foglia, T. A. *J. Am. Oil Chem. Soc.* **2006**, *83*, 629-634.

71. Metathesis of Unsaturated Fatty Esters. Verkuijlen, E.; Boelhouwer, C. *Fette, Seifen, Anstrichmittel* **1976**, *78*, 444-447.

72. Synthesis of Long Chain Unsaturated α,ω-Dicarboxylic Acids from Renewable Materials via Olefin Metathesis. Ngo, H. L.; Foglia, T. A. *J. Am. Oil Chem. Soc.* **2007**, *84*, 777-784.

73. Aliphatic Long-Chain C20 Polyesters from Olefin Metathesis. Trzaskowski, J.; Quinzler, D.; Bährle, C.; Mecking, S. *Macromol. Rapid Commun.* **2011**, *32*, 1352-1356.

74. Polymers and surfactants on the basis of renewable resources. Warwel, S.; Brüse, F.; Demes, C.; Kunz, M.; Rüsch gen. Klaas, M. *Chemosphere* **2001**, *43*, 39-48.

75. New Polymers from Plant Oil as Raw Material. Warwel, S.; Brüse, F.; Kunz, M. *Fresenius' Environ. Bull.* **2003**, *12*, 534-539.

76. Renewable Monomer Feedstocks via Olefin Metathesis: Fundamental Mechanistic Studies of Methyl Oleate Ethenolysis with the First-Generation Grubbs Catalyst. Burdett, K. A.; Harris, L. D.; Margl, P.; Maughon, B. R.; Mokhtar-Zadeh, T.; Saucier, P. C.; Wasserman, E. P. *Organometallics* **2004**, *23*, 2027-2047.

77. A Stable Ruthenium Catalyst for Productive Olefin Metathesis. Forman, G. S.; McConnell, A. E.; Hanton, M. J.; Slawin, A. M. Z.; Tooze, R. P.; van Rensburg, W. J.; Meyer, W. H.; Dwyer, C.; Kirk, M. M.; Serfontein, D. W. *Organometallics* **2004**, *23*, 4824-4827.

78. Metathesis of Renewable Unsaturated Fatty Acid Esters Catalysed by a Phoban-indenylidene Ruthenium Catalyst. Forman, G. S.; Bellabarba, R. M.; Tooze, R. P.; Slawin, A. M. Z.; Karch, R.; Winde, R. *J. Organomet. Chem.* **2006**, *691*, 5513-5516.

79. Ruthenium Olefin Metathesis Catalysts for the Ethenolysis of Renewable Feedstocks. Schrodi, Y.; Ung, T.; Vargas, A.; Mkrtumyan, G.; Lee, C. W.; Champagne, T. M.; Pederson, R. L.; Hong, S. H. *Clean* **2008**, *36*, 669-673.

80. Kinetic Selectivity of Olefin Metathesis Catalysts Bearing Cyclic (Alkyl)(Amino)Carbenes. Anderson, D. R.; Ung, T.; Mkrtumyan, G.; Bertrand, G.; Grubbs, R. H.; Schrodi, Y. *Organometallics* **2008**, *27*, 563-566.

81. Ethenolysis of Methyl Oleate in Room-Temperature Ionic Liquids. Thurier, C.; Fischmeister, C.; Bruneau, C.; Olivier-Bourbigou, H.; Dixneuf, P. H. *ChemSusChem* **2008**, *1*, 118-122.

82. Ethenolysis Reactions Catalyzed by Imido Alkylidene Monoaryloxide Monopyrrolide (MAP) Complexes of Molybdenum. Marinescu, S. C.; Schrock, R. R.; Müller, P.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2009**, *131*, 10840-10841.

83. Highly Selective Ruthenium Metathesis Catalysts for Ethenolysis. Thomas, R. M.; Keitz, B. K.; Champagne, T. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **2011**, *133*, 7490-7496.

84. Cyclic Alkyl Amino Carbene (CAAC) Ruthenium Complexes as Remarkably Active Catalysts for Ethenolysis. Marx, V. M.; Sullivan, A. H.; Melaimi, M.; Virgil, S. C.; Keitz, B. K.; Weinberger, D. S.; Bertrand, G.; Grubbs, R. H. *Angew. Chem. Int. Ed.* **2015**, *54*, 1919-1923.

85. Development of a Green Process for Poly-α-olefin Based Lubricants. Yadav, G. D.; Doshi, N. S. *Green Chem.* **2002**, *4*, 528-540.

86. Polyesters by Lipase-Catalyzed Polycondensation of Unsaturated and Epoxidized Long-Chain α,ω-Dicarboxylic Acid Methyl Esters with Diols. Warwel, S.; Demes, C.; Steinke, G. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 1601-1609.

87. Polyesters of ω-Unsaturated Fatty Acid Derivatives. Warwel, S.; Tillack, J.; Demes, C.; Kunz, M. *Macromol. Chem. Phys.* **2001**, *202*, 1114-1121.

88. Cross-Metathesis of Unsaturated Natural Oils with 2-Butene. High Conversion and Productive Catalyst Turnovers. Patel, J.; Elaridi, J.; Jackson, W. R.; Robinson, A. J.; Serelis, A. K.; Such, C. *Chem. Commun.* **2005**, 5546-5547.

89. High Conversion and Productive Catalyst Turnovers in Cross-Metathesis Reactions of Natural Oils with 2-Butene. Patel, J.; Mujcinovic, S.; Jackson, W. R.; Robinson, A. J.; Serelis, A. K.; Such, C. *Green Chem.* **2006**, *8*, 450-454.

90. Synthesis of Terminal Alkenes from Internal Alkenes via Olefin Metathesis. Schrodi, Y.; Pederson, R. L.; Kaido, H.; Tupy, M. J. (Materia Inc.), WO 2008/046106 A2 (**2008**).

91. Refining of Plant Oils to Chemicals by Olefin Metathesis. Chikkali, S.; Mecking, S. *Angew. Chem. Int. Ed.* **2012**, *51*, 5802-5808.

92. Methods of Refining and Producing Fuel from Natural Oil Feedstocks. Cohen, S. A.; Luetkens, M. L.; Balakrishnan, C.; Snyder, R. (Elevance Renewable Sciences), WO 2011/046872 A2 (**2011**).

93. Form S1 SEC filing by Elevance Renewable Sciences of September 20, 2011 (IPO registration).

94. a) Press release by Elevance Renewable Sciences of July 18, 2013. b) Press release by Wilmar International of July 18, 2013.

95. a) Press release by Elevance Renewable Sciences of October 22, 2013 b) Press release by Elevance Renewable Sciences of February 5, 2014.

96. a) Press release by Elevance Renewable Sciences of September 17, 2013. b) Inherent™ C_{18} diacid. Beuhler, A. *Bioplastics Magazine* **2013**, *8*, 8-10.

97. Isomerizing Hydroformylation of Fatty Acid Esters: Formation of ω-Aldehydes. Behr, A.; Obst, D.; Westfechtel, A. *Eur. J. Lipid Sci. Technol.* **2005**, *107*, 213-219.

98. Highly Selective Tandem Isomerization-Hydroformylation Reaction of Trans-4-octene to n-Nonanal with Rhodium-BIPHEPHOS Catalysis. Behr, A.; Obst, D.; Schulte, C.; Schosser, T. *J. Mol. Catal. A: Chem.* **2003**, *206*, 179-184.
99. Tandem Isomerization/Hydroformylation/Hydrogenation of Internal Alkenes to n-Alcohols Using Rh/Ru Dual- or Ternary-Catalyst Systems. Yuki, Y.; Takahashi, K.; Tanaka, Y.; Nozaki, K. *J. Am. Chem. Soc.* **2013**, *135*, 17393-17400.
100. Isomerizing-Hydroboration of the Monounsaturated Fatty Acid Ester Methyl Oleate. Ghebreyessus, K. Y.; Angelici, R. J. *Organometallics* **2006**, *25*, 3040-3044.
101. Iridium-Catalyzed Hydroboration of Alkenes with Pinacolborane. Yamamoto, Y.; Fujikawa, R.; Umemoto, T.; Miyaura, N. *Tetrahedron* **2004**, *60*, 10695-10700.
102. An Efficient and Recyclable Catalytic System Comprising Nano-Iridium(0) and a Pyridinium Salt of nido-Carboranyldiphosphine for the Synthesis of One-Dimensional Boronate Esters via Hydroboration Reaction. Zhu, Y.; Jang, S. H. A.; Tham, Y. H.; Algin, O. B.; Maguire, J. A.; Hosmane, N. S. *Organometallics* **2012**, *31*, 2589-2596.
103. The Addition of Silicon Hydrides to Olefinic Double Bonds. Part I. The Use of Phenylsilane, Diphenylsilane, Phenylmethylsilane, Amylsilane and Tribromosilane. Speier, J. L.; Zimmerman, R.; Webster, J. *J. Am. Chem. Soc.* **1956**, *78*, 2278-2281.
104. The Addition of Silicon Hydrides to Olefinic Double Bonds. Part II. The Use of Group VIII Metal Catalysts. Speier, J. L.; Webster, J. A.; Barnes, G. H. *J. Am. Chem. Soc.* **1957**, *79*, 974-979.
105. Iridium-Catalysed Isomerising Trialkylsilylation of Methyl Oleate. Huber, T.; Firlbeck, D.; Riepl, H. M. *J. Organomet. Chem.* **2013**, *744*, 144-148.
106. Tandem Isomerisation-Carbonylation Catalysis: Highly Active Palladium(II) Catalysts for the Selective Methoxycarbonylation of Internal Alkenes to Linear Esters. Pugh, R. I.; Drent, E.; Pringle, P. G. *Chem. Commun.* **2001**, 1476-1477.
107. Highly Selective Formation of Linear Esters from Terminal and Internal Alkenes Catalysed by Palladium Complexes of Bis-(di-*tert*-butylphosphinomethyl)benzene. Jiménez-Rodriguez, C.; Foster, D. F.; Eastham, G. R.; Cole-Hamilton, D. J. *Chem. Commun.* **2004**, 1720-1721.
108. Dicarboxylic Acid Esters from the Carbonylation of Unsaturated Esters under Mild Conditions. Jiménez-Rodriguez, C.; Eastham, G. R.; Cole-Hamilton, D. J. *Inorg. Chem. Commun.* **2005**, *8*, 878-881.
109. Linear Semicrystalline Polyesters from Fatty Acids by Complete Feedstock Molecule Utilization. Quinzler, D.; Mecking, S. *Angew. Chem. Int. Ed.* **2010**, *49*, 4306-4308.

110. Polymer Precursors from Catalytic Reactions of Natural Oils. Furst, M. R. L.; Le Goff, R.; Quinzler, D.; Mecking, S.; Botting, C. H.; Cole-Hamilton, D. J. *Green Chem.* **2012**, *14,* 472-477.

111. α,ω-Functionalized C_{19} Monomers. Walther, G.; Deutsch, J.; Martin, A.; Baumann, F.-E.; Fridag, D.; Franke, R.; Köckritz, A. *ChemSusChem* **2011**, *4*, 1052-1054.

112. Long-Chain Linear C_{19} and C_{23} Monomers and Polycondensates from Unsaturated Fatty Acid Esters. Stempfle, F.; Quinzler, D.; Heckler, I.; Mecking, S. *Macromolecules* **2011**, *44*, 4159-4166.

113. Mechanistic Features of Isomerizing Alkoxycarbonylation of Methyl Oleate. Roesle, P.; Dürr, C. J.; Möller, H. M.; Cavallo, L.; Caporaso, L.; Mecking, S. *J. Am. Chem. Soc.* **2012**, *134*, 17696-17703.

114. A Comprehensive Mechanistic Picture of the Isomerizing Alkoxycarbonylation of Plant Oils. Roesle, P.; Caporaso, L.; Schnitte, M.; Goldbach, V.; Cavallo, L.; Mecking, S. *J. Am. Chem. Soc.* **2014**, *136*, 16871-16881.

115. Catalyst Activity and Selectivity in the Isomerising Alkoxycarbonylation of Methyl Oleate. Christl, J. T.; Roesle, P.; Stempfle, F.; Wucher, P.; Göttker-Schnetmann, I.; Müller, G.; Mecking, S. *Chem. Eur. J.* **2013**, *19*, 17131-17140.

116. Promotion of Selective Pathways in Isomerizing Functionalization of Plant Oils by Rigid Framework Substituents. Christl, J. T.; Roesle, P.; Stempfle, F.; Müller, G.; Caporaso, L.; Cavallo, L.; Mecking, S. *ChemSusChem* **2014**, *7*, 3491-3495.

117. Long-Chain Polyesters via Chemical Catalytic Conversions of Fatty Acid Esters. Stempfle, F.; Roesle, P.; Mecking, S. In *ACS Symp. Ser.: Biobased Monomers, Polymers and Materials* (Eds.: Richard A. Gross, Patrick B. Smith), **2012**, *1105*, 151-164.

118. Polymerisable Di- and Triesters from Tall Oil Fatty Acids and related compounds. Furst, M. R. L.; Seidensticker, T.; Cole-Hamilton, D. J. *Green Chem.* **2013**, *15*, 1218-1225.

119. Unsymmetrical α,ω-Difunctionalized Long-Chain Compounds via Full Molecular Incorporation of Fatty Acids. Witt, T.; Stempfle, F.; Roesle, P.; Häußler, M.; Mecking, S. *ACS Catal.* **2015**, *5*, 4519-4529.

120. Fakirov, S., *Transreactions in condensation polymers*. Wiley-VCH: Weinheim; New York, **1999**.

121. Rogers, M. E.; Long, T. E. *Synthetic methods in step-growth polymers*. Wiley-Interscience: Hoboken, N.J., **2003**.

122. Polymers and Polyfunctionality. Carothers, W. H. *Trans. Faraday Soc.* **1936**, *32*, 39-49.

123. Polyesters. Köpnick, H.; Schmidt, M.; Brügging, W.; Rüter, J.; Kaminsky, W., In *Ullmann's Encyclopedia of Industrial Chemistry*, Gerhartz, W.; Elvers, B. (Eds.) Wiley-VCH: Weinheim, **2000**.

124. Poly(triacontamethy1ene triacontanedioate) as Polyethylene Analogue: Properties and Enzymatic Degradation. Cho, I.; Lee, K. *Macromol. Chem. Phys.* **1997**, *198*, 861-869.
125. Polymers from Fatty Acids: Poly(ω-hydroxyl tetradecanoic acid) Synthesis and Physico-Mechanical Studies. Liu, C.; Cai, J.; Xie, W.; Long, T. E.; Turner, S. R.; Lyons, A.; Gross, R. A. *Biomacromolecules* **2011**, *12*, 3291-3298.
126. Changes in the Chemical Composition of Essential Oil of *Angelica Archangelica L.* Roots during Storage. Nivinskiene, O.; Butkiene, R.; Mockute, D. *Chemija* **2003**, *14*, 52-56.
127. Crystallization in High Polymers. V. Dependence of Melting Temperatures of Polyesters and Polyamides on Composition and Molecular Weight. Evans, R. D.; Mighton, H. R.; Flory, P. J. *J. Am. Chem. Soc.* **1950**, *72*, 2018-2028.
128. Korshak, V. V.; Vinogradova, S. V. *Polyesters*; Pergamon Press: Oxford, U.K., **1965**.
129. Thermodynamic Quantities Governing Melting. Mandelkern, L.; Alamo, R. G. In *Physical Properties of Polymers Handbook*; Mark, J. E. (Ed.); Springer: New York, **2007**; pp 165-186.
130. Which Polyesters Can Mimic Polyethylene? Stempfle, F.; Ortmann, P.; Mecking, S. *Macromol. Rapid Commun.* **2013**, *34*, 47-50.
131. Synthesis of Aliphatic Suberin-Like Polyesters by Ecofriendly Catalytic Systems. Sousa, A. F.; Silvestre, A. J. D.; Gandini, A.; Neto, C. P. *High Perform. Polym.* **2012**, *24*, 4-8.
132. Growth and Morphology of Single Crystals of Linear Aliphatic Polyesters. Kanamoto, T.; Tanaka, K.; Nagai, H. *J. Polym. Sci., Part A-2: Polym. Phys.* **1971**, *9*, 2043-2060.
133. Synthesis and Characterization of Aliphatic Unsaturated Polyesters from Trans-4-octene-1,8-dioic and Trans-3-hexene-1,6-dioic Acids. Maglio, G.; Marchetta, C.; Botta, A.; Palumbo, R.; Pracella, M. *Eur. Polym. J.* **1979**, *15*, 695-699.
134. Physical Characterization of Sorbitol or Glycerol Containing Aliphatic Copolyesters Synthesized by Lipase-Catalyzed Polymerization. Fu, H.; Kulshrestha, A. S.; Gao, W.; Gross, R. A.; Baiardo, M.; Scandola, M. *Macromolecules* **2003**, *36*, 9804-9808.
135. Single Crystal Morphology and Structural Data of a Series of Polyesters Derived from 1,8-Octanediol. Gestí, S.; Casas, M. T.; Puiggali, J. *Eur. Polym. J.* **2008**, *44*, 2295-2307.
136. Polymeric Vehicle for High Solids Coatings. Frank, N. J.; Shou-Kuan, F.; Jun, H.; Xiaoying, Y. (Eastern Michigan University), U.S. Patent 5,641,854 (**1997**).
137. Synthetic Absorbable Surgical Devices of Poly(alkylene oxalates). Shalaby, W.; Damiolkowski, D. (Ethicon, Inc.), U.S. Patent 4,140,678 (**1979**).
138. Molecular Packing of Polyesters Derived from 1,4-Butanediol and Even Aliphatic Dicarboxylic Acids. Almontassir, A.; Gestí, S.; Franco, L.; Puiggalí, J. *Macromolecules* **2004**, *37*, 5300-5309.

139. Thermodynamics of the Phase Behaviour of Poly(vinyl chloride)/Aliphatic Polyester Blends. Woo, E. M.; Barlow, J. W.; Paul, D. R. *Polymer* **1985**, *26*, 763-773.

140. Polymers Made of Renewable Resources. Mecking, S.; Quinzler, D.; WO 2011/089256 A1 (**2011**).

141. Aliphatic Polyesters: "Bionolle". Ishioka, R.; Kitakuni, E.; Ichikawa; Y. In *Biopolymers*; Steinbüchel, A.; Doi, Y. (Eds.); Wiley-VCH: Weinheim, **2002**; Vol. 4, 275-297

142. Moisture-Curing Hot-Melt Adhesive with Good Adhesion. Brenner, G.; Koschabek, R. (Evonik Degussa GmbH), WO 2009/010324 A2 (**2009**).

143. Communication 69: Properties of Polyesters formed by Dicarboxylic Acids with Some Polymethylene Glycols. Korshak, V. V.; Vinogradova, S. V.; Vlasova, E. S. *Russ. Chem. Bull.* **1954**, *3*, 949-955.

144. Studies on Polymerization and Ring Formation. II. Polyesters. Carothers, W. H.; Arvin, J. A. *J. Am. Chem. Soc.* **1929**, *51*, 2560-2570.

145. Polyethylene Like Polymers. Aliphatic Polyesters of Dodecanedioic Acid: 1. Synthesis and Properties. Barbiroli, G.; Lorenzetti, C.; Berti, C.; Fiorini, M.; Manaresi, P. *Eur. Polym. J.* **2003**, *39*, 655-661.

146. Feuchtigkeitshärtende Schmelzklebstoffe, Verfahren zu deren Herstellung und deren Verwendung. Brand, T.; Brenner, G.; Franzmann, G.; Zagefka, H.-D. (Degussa AG), WO 2005/090428 A1 (**2005**).

147. Communication 63: Polyesters of 1,20-Eicosanediol. Korshak, W. V.; Vinogradova, S. V. *Russ. Chem. Bull.* **1953**, *2*, 995-998.

148. X-Ray Investigation of the Decamethylene Series of Polyester. Fuller, C. S.; Frosch, C. J., J. Am. Chem. Soc. 1939, 61, 2575-2580.

149. The Melting Points of Chain Polymers. Bunn, C. W. *J. Polym. Sci.* **1955**, *16*, 323-343.

150. Epitaxial Crystallization of Polyesters on Inorganic and Organic Substrates. Rickert, S. E.; Baer, E.; Wittmann, J. C.; Kovacs, A. J. *J. Polym. Sci., Polym. Phy. Ed.* **1978**, *16*, 895-906.

151. Crystals Structure Morphology and Defects. Wunderlich, B. *Macromolecular Physics: Vol. 1.* New York: Academic Press, **1973**.

152. Long-Spaced Aliphatic Polyesters. Ortmann, P.; Mecking, S. *Macromolecules* **2013**, *46*, 7213-7218.

153. From Polyethylene to Polyester: Influence of Ester Groups on the Physical Properties. Pepels, M. P. F.; Hansen, M. R.; Goossens, H.; Duchateau, R., *Macromolecules* **2013**, *46*, 7668-7677.

154. Encoding Crystal Microstructure and Chain Folding in the Chemical Structure of Synthetic Polymers. Le Fevere de Ten Hove, C.; Penelle, J.; Ivanov, D. A.; Jonas, A. M., *Nat. Mater.* **2004**, *3*, 33-37.
155. Catalytic Ring-Opening Polymerization of Renewable Macrolactones to High Molecular Weight Polyethylene-like Polymers. Van der Meulen, I.; Gubbels, E.; Huijser, S.; Sablong, R. l.; Koning, C. E.; Heise, A.; Duchateau, R. *Macromolecules* **2011**, *44*, 4301-4305.
156. Nature's Polyethylene. Cole-Hamilton, D. J. *Angew. Chem. Int. Ed.* **2010**, *49*, 8564-8568.
157. Real-Time Structure Changes during Uniaxial Stretching of Poly(ω-pentadecalactone) by in Situ Synchrotron WAXD/SAXS Techniques. Cai, J.; Hsiao, B. S.; Gross, R. A. *Macromolecules* **2011**, *44*, 3874-3883.
158. Characterization of Long-Chain Aliphatic Polyesters: Crystalline and Supramolecular Structure of PE22,4 Elucidated by X-ray Scattering and Nuclear Magnetic Resonance. Menges, M. G.; Penelle, J.; Le Fevere de Ten Hove, C.; Jonas, A. M.; Schmidt-Rohr, K., *Macromolecules* **2007**, *40*, 8714-8725.
159. ω-Pentandecalactone Polymerization and ω-Pentadecalactone/ε-Caprolactone Co-Polymerization Reactions Using Organic Catalysts. Bouyahyi, M.; Pepels, M. P. F.; Heise, A.; Duchateau, R. *Macromolecules* **2012**, *45*, 3356-3366
160. Cocrystallization of Random Copolymers of ω-Pentadecalactone and ε-Caprolactone Synthesized by Lipase Catalysis. Ceccorulli, G.; Scandola, M.; Kumar, A.; Kalra, B.; Gross, R. A. *Biomacromolecules* **2005**, *6*, 902-907.
161. Physical Characterization of Poly(ω-pentadecalactone) Synthesized by Lipase-Catalyzed Ring-Opening Polymerization. Letizia Focarete, M.; Scandola, M.; Kumar, A.; Gross, R. A., *J. Polym. Sci., Part B: Polym. Phys.* **2001**, *39*, 1721-1729.
162. Effects of Molecular Weight on Poly(ω-pentadecalactone) Mechanical and Thermal Properties. Cai, J.; Liu, C.; Cai, M.; Zhu, J.; Zuo, F.; Hsiao, B. S.; Gross, R. A. *Polymer* **2010**, *51*, 1088-1099.

2 Scope of the thesis

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. In view of dwindling fossil resources and a surging energy demand an increased utilization of alternative renewable resources is desirable on the long term. More importantly, the unique molecular structure of different (biomass) substrates can also provide otherwise inaccessible products and properties.

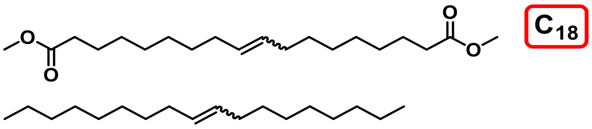
In this regard fatty acids from plant oils are attractive substrates for monomer generation. The incorporation of their long-chain methylene sequences into aliphatic polymer chains results in polyethylene-like crystal phases and high melting points, advantageous for thermoplastic processing. To date, such materials have been generated from ring-opening polymerization of certain large ring lactones. This fundamentally limits their availability and the length of the long-chain repeat units. Recently, novel catalytic transformations have been devised for the syntheses of long-chain, α,ω-functionalized monomers, which provide a perspective for making them practically accessible.

In this thesis the scope of these novel polycondensation monomers is explored. For this purpose various α,ω-functionalized compounds starting from common seed oils are prepared in polymerization grade purity (≥ 99 %) and subsequently transformed into the corresponding long-chain aliphatic polycondensates. Besides thermal properties, the tensile and elastomeric material properties of these novel materials are of particular interest. Moreover as the utilization of biomass from land plants raises urgent issues such as consumption of land and irrigation water, as well as competition with food production, also the synthesis of long-chain aliphatic polycondensates from algae oil with its distinctly different fatty acid spectrum is investigated.

3 Long-chain polycondensation monomers by self-metathesis of unsaturated fatty acids

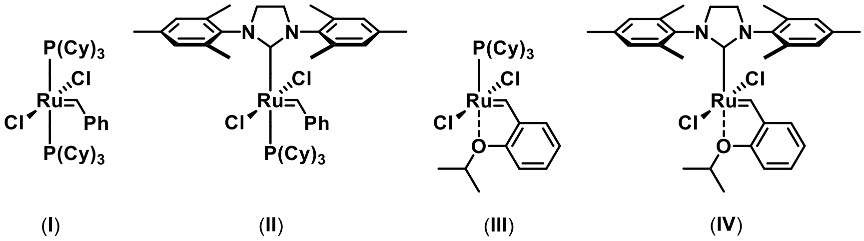
3.1 Introduction

The first successful self-metathesis transformations of unsaturated fatty esters into mono-unsaturated hydrocarbons and α,ω-diesters were reported by Boelhouwer *et al.* in 1974. Using $WCl_6/SnMe_4$ methyl oleate and its trans analogue methyl elaidate were converted to dimethyl-1,18-octadec-9-enedioate and octadec-9-ene, reaching equilibrium conversion within a few hours (**Scheme 3.1**).[1]



Scheme 3.1: Reaction products from the self-metathesis of methyl oleate.

Subsequently, several other classical *in situ* catalyst systems and also heterogeneous catalysts were found to convert unsaturated fatty acids and oil substrates.[2] However, their performance in these reactions is limited. This has been suggested to be a consequence of a limited tolerance towards the substrates' carboxylic acid or ester groups.[3] This issue was advanced with the development of more functional group tolerant isolated metal alkylidene metathesis catalyst precursors (**Scheme 3.2**).[4]



Scheme 3.2: Ruthenium based metathesis catalysts.

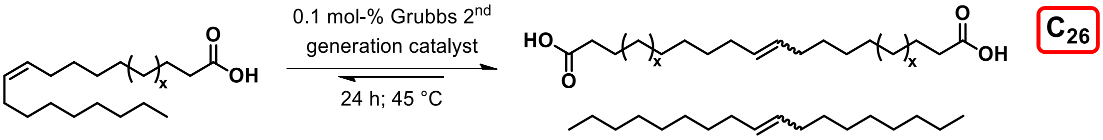
In particular ruthenium alkylidenes, most prominently [$(PCy_3)_2Cl_2Ru=CHPh$] (Grubbs 1st generation catalyst; **I**) and [$(PCy_3)(\eta$-C-$C_3H_4N_2Mes_2)Cl_2Ru=CHPh$] (Grubbs 2nd generation catalyst; **II**) have been found to be very active catalyst precursors. High productivities of up to several 10^5 turnovers have been reported for the self-metathesis of methyl oleate, applying these catalysts.[5] Nevertheless, molar conversions are limited (at its best ≈ 50 %), since such reactions typically are subject to thermodynamic control. This limitation could be overcome applying solvent-free self-metathesis of monounsaturated fatty acids. Under these bulk conditions the diacid products formed during the reaction are not soluble in the reaction medium and precipitate from the mixture. This removal of a product shifts the equilibrium mixture. Thus, conversion of the starting material and yields of the diacid products increase. In this way even carbon numbered, monounsaturated dicarboxylic acids (C_{18} - C_{26}) can be obtained.[6] Note that self-metathesis is also a relevant side-reaction of the industrial butenolysis of plant oils described in more detail in chapter 1.3.2 and thus its products are available from this process.

Within this thesis preparation and isolation of such long-chain dicarboxylic acids in polymerization grade purity (> 99 %) is presented. Furthermore, after hydrogenation of the double bond and subsequent reduction to the corresponding diols, these α,ω-difunctional compounds are utilized for the synthesis of long-chain aliphatic polyesters.

3.2 Results and discussion

3.2.1 Long-chain α,ω-difunctional compounds by self-metathesis of unsaturated fatty acids

Among conveniently available fatty acid starting materials, erucic acid, which can be obtained from the seed oil of some rapeseeds or in particular from crambe,[7] stands out by its long chain length of 22 carbon atoms. Of the different possibilities for conversions into α,ω-difunctional products presented above, olefin metathesis yields longer chain products *vs.* isomerizing alkoxycarbonylation[8] or ω-oxidation[9] due to the unsymmetric placement of the double bond at C-13. By self-metathesis with Grubbs' second-generation ruthenium alkylidene[6,10] technical grade erucic acid can be converted into stoichiometric amounts of 1,26-hexacos-13-enedioic acid and octadec-9-ene (**Scheme 3.3**).



Scheme 3.3: Solvent-free self-metathesis of erucic acid (x=5).

In our hands however, applying these reaction conditions, isomerization of the double bond was observed, as exemplified here by the gas chromatogram of the hydrocarbon section (**Figure 3.1**).

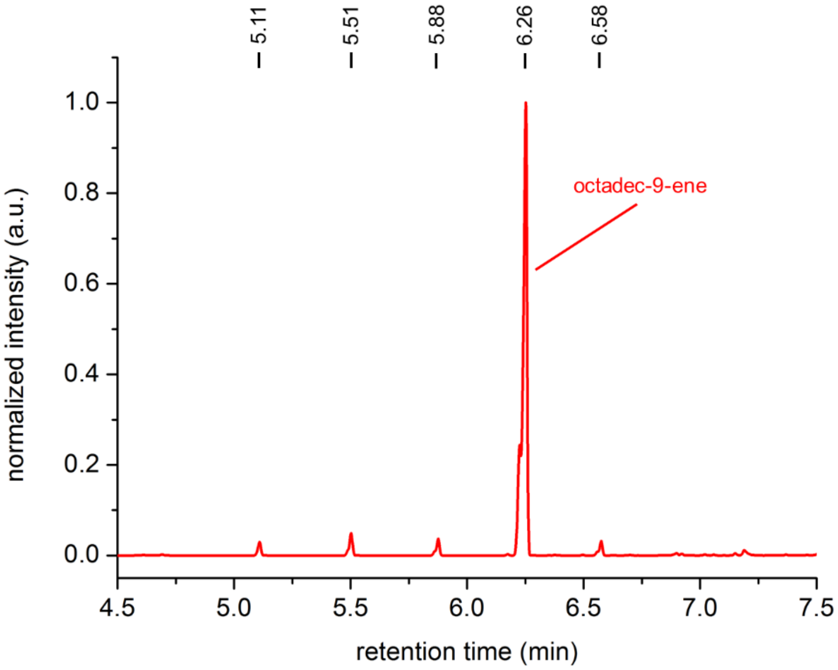


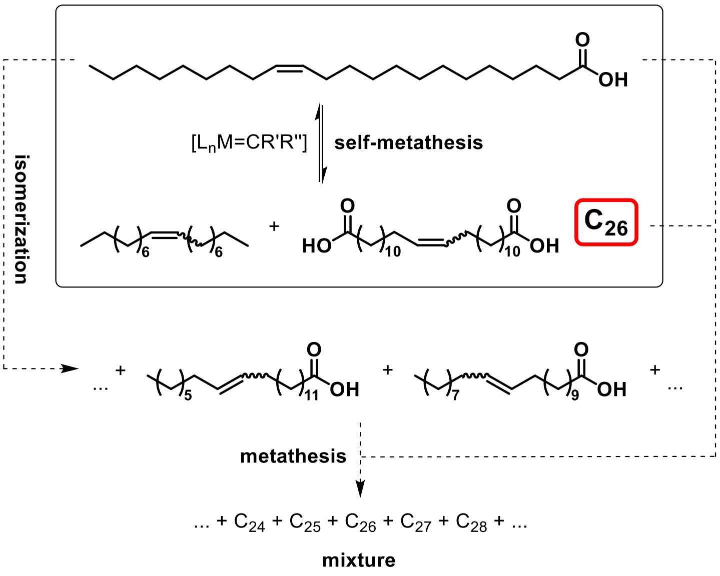
Figure 3.1: Gas chromatogram of the hydrocarbon fraction.

Besides the expected main product octadec-9-ene, also pentadec-6-ene, hexadec-7-ene, heptadec-8-ene and nonadec-9-ene could be identified by means of GC-MS (**Table 3.1**).

Table 3.1: Hydrocarbon fraction after self-metathesis of erucic acid.

entry	retention time	m_z [g mol^{-1}]	systematic name	area [%]
1	5.11 min	210.2	pentadec-6-ene (C_{15})	1.9
2	5.51 min	224.2	hexadec-7-ene (C_{16})	3.3
3	5.88 min	238.2	heptadec-8-ene (C_{17})	2.5
4	6.26 min	252.3	octadec-9-ene (C_{18})	90.1
5	6.58 min	266.3	nonadec-9-ene (C_{19})	2.2

Such monounsaturated hydrocarbons, as well as, a range of monoesters and α,ω-diesters with different chain lengths, are formed due to cross-metathesis of double bond isomers generated by both isomerization of the substrate and of primary metathesis products (**Scheme 3.4**).



Scheme 3.4: Self-metathesis of erucic acid and isomerization as possible side reaction.

Double bond isomerization is a generic issue in olefin metathesis transformations[11] and is catalyzed by decomposition products of the metal alkylidene catalyst.[12] As a complete separation of these byproducts is likely not practicable, this side reaction is a crucial issue. However, selectivity towards the desired products can be increased by optimizing the reaction conditions such as choice of the metathesis catalyst, temperature or reaction time. Yet hardly no conversion to the desired product was observed changing the metathesis catalyst from Grubbs 2nd generation catalyst (**II**) to Grubbs 1st generation catalyst (**I**) or Hoveyda-Grubbs catalyst 1st generation (**III**). Conversions also drastically dropped by decreasing the catalyst concentration from 0.1 mol-% to 0.01 mol-%, whereas higher catalyst concentrations did not increase the conversion and just led to a decrease in selectivity to the desired 1,26-diacid (cf. **Table 3.2**, entry 1,2 and 4).

Table 3.2: Self-metathesis of erucic acid applying different catalyst concentrations.[a]

entry	catalyst concentration [mol-%]	conversion[b] [%]	Selectivity[b] [%]
1	0.01	< 1	n.d.
2	0.1	58	92
3	0.1[c]	57	93
4	1	50	90

[a] Erucic acid (2 g, 5.9 mmol) Grubbs 2nd generation catalyst; 45 °C, 1 h.
[b] Selectivity for the primary metathesis product octadec-9-ene, determined by GC analysis of the crude reaction mixture.
[c] addition of 1 mol-% tetrachloro-1,4-benzoquinone.

Furthermore, double bond migration can be also reduced in the presence of different additives such as benzoquinones or acids by preventing catalyst decomposition or scavenging the catalyst decomposition products.[13] For the self-metathesis of erucic acid however, no positive effect on the selectivity was observed by addition of 1 mol-% tetrachloro-1,4-benzoquinone. Conversion and selectivity still remained in the same order of magnitude compared to the comparative experiment without any additives (cf. **Table 3.2**, entry 2 and 3).

Best results were achieved by reducing the reaction time to about 15 minutes under otherwise identical conditions, as exemplified here by the gas chromatogram of the hydrocarbon section (**Figure 3.2**).

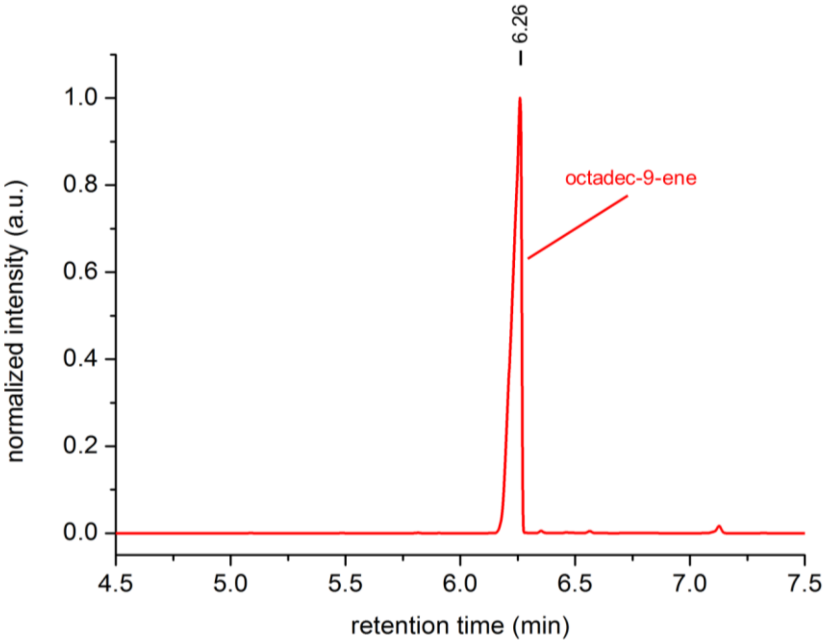


Figure 3.2: Gas chromatogram of the hydrocarbon fraction under optimized reaction conditions (0.1 mol-% Grubbs 2nd generation catalyst; 45 °C, 15 min).

The desired primary metathesis product octadec-9-ene was obtained with a selectivity of ca. 99 %. In this way after purification of the crude product by esterification and subsequent recrystallization, the desired C_{26} diacid could be isolated in pure form (> 99 %), as illustrated by gas chromatographic analysis after hydrogenation to dimethyl-1,26-hexacosanedioate (**Figure 3.3**).

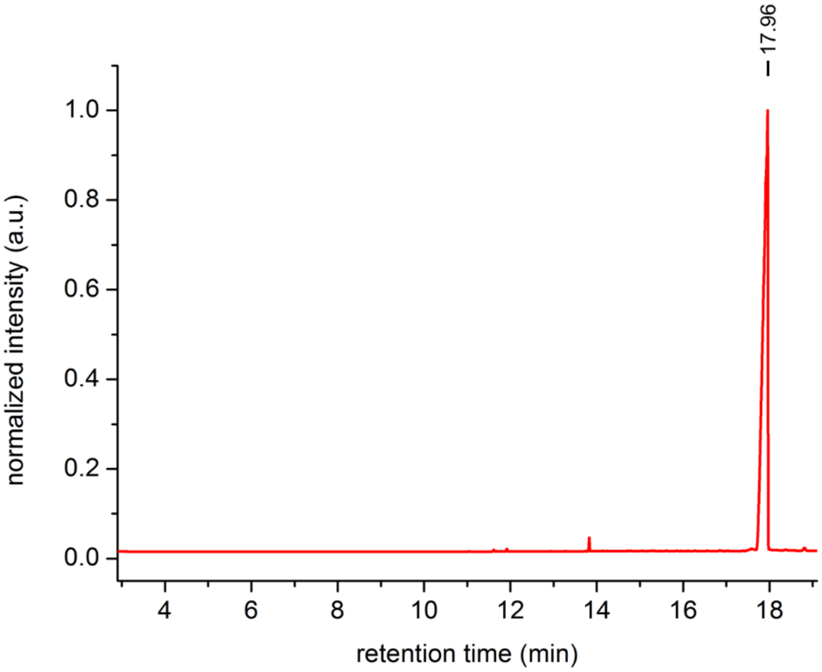
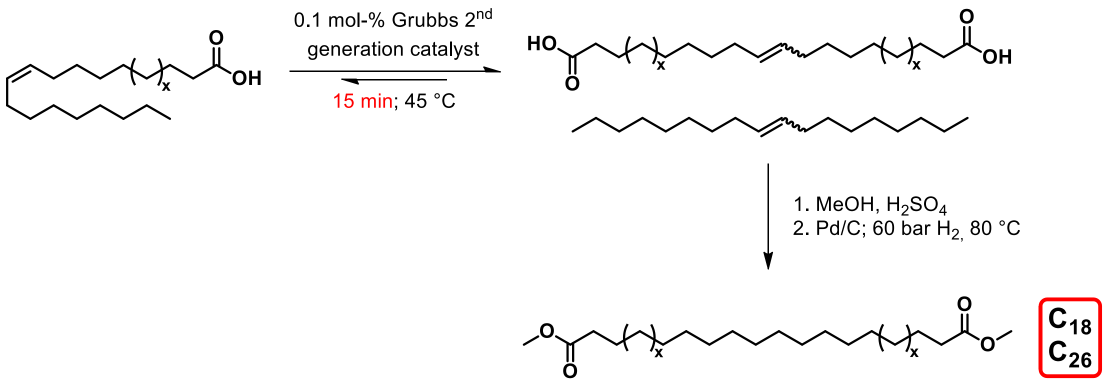


Figure 3.3: Gas chromatogram of pure dimethyl-1,26-hexacosanedioate (≥ 99 % purity).

Applying this reaction sequence of self-metathesis and exhaustive hydrogenation to technical grade oleic acid also pure dimethyl-1,18-octadecanedioate can be synthesized (**Scheme 3.5**).



Scheme 3.5: Solvent-free self-metathesis followed by exhaustive hydrogenation of the double bond as a preparative route to linear α,ω-difunctional monomers starting from oleic acid (x=1) or erucic acid (x=5).

Alternatively the shorter chain C_{18}-compound can be generated by ω-oxidation of stearic acid. 1,18-Octadecanedioic acid from this source is marketed by Emery Oleochemicals under the trade name Emerox118®.[14] Gas chromatographic analysis of the commercial product exhibited a purity of about 92 %. These impurities could be removed by tranesterification with methanol and subsequent recrystallization. Thus, in this way also pure (> 99 % from GC) dimethyl-1,18-octadecanedioate could be obtained.

The corresponding long-chain α,ω-diols were generated by reduction of the aforementioned diesters, stoichiometrically with $LiAlH_4$ or by catalytic hydrogenation with Saudan's[15] ruthenium catalyst.

3.2.2 Synthesis of Polyester-26.26 and Polyester-18.18

Polycondensation of these difunctional A_2+B_2 monomers catalyzed by titanium alkoxides afforded the corresponding long-chain aliphatic polyesters, namely poly[1,26-hexacosanediyl-1,26-hexacosanedioate] (**PE-26.26**) and poly[1,18-octadecanediyl-1,18-octadecanedioate] (**PE-18.18**).

Table 3.3: Molecular weights and thermal properties of long-chain aliphatic polyesters.

entry	T_m[a] [°C]	T_c[a] [°C]	$M_{n,NMR}$[b] [g mol^{-1}]	$M_{n,GPC}$[c] [g mol^{-1}]	M_w/M_n[c]
PE-26.26	114	94	2.0×10^4	2.4×10^4	2.6
PE-18.18	100	77	3.2×10^4	3.7×10^4	2.4

[a] Determined by DSC with a heating/cooling rate of 10 K min^{-1}.
[b] Determined by end-group analysis from ^{1}H-NMR spectroscopy.
[c] Determined by GPC at 160 °C in trichlorobenzene *vs.* polyethylene standards.

End-group analysis by ^{1}H-NMR spectroscopy (cf. **Chapter 3.4.3**), as well as high temperature GPC measurements relative to polyethylene standards, revealed number-average molecular weights on the order of several 10^4 g mol^{-1} (**Table 3.3**).

As determined by DSC **PE-18.18** exhibits a melting point of T_m = 100 °C (T_c = 77 °C, ΔH_m = 153 J g^{-1}). Thus thermal properties of this long-chain aliphatic polyester already 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. For the even longer chain aliphatic polyester **PE-26.26** a melting point of T_m = 114 °C (T_c = 94 °C, ΔH_m = 160 J g^{-1}) was found. This is the highest melting point observed for an aliphatic mid- or long-chain polyester to date to our knowledge.[a] Within experimental error, this value agrees with data reported for polyester-30.30 (accessible by multistep monomer syntheses).[16] In parallel to this work, Meier and co-workers[17] communicated the preparation of polyester-26.26 via an essentially identical approach. They reported a somewhat lower T_m of 104 °C. Also for polyester-18.18 a lower melting point of 95 °C can be found in literature.[18] Here, however as already mentioned by

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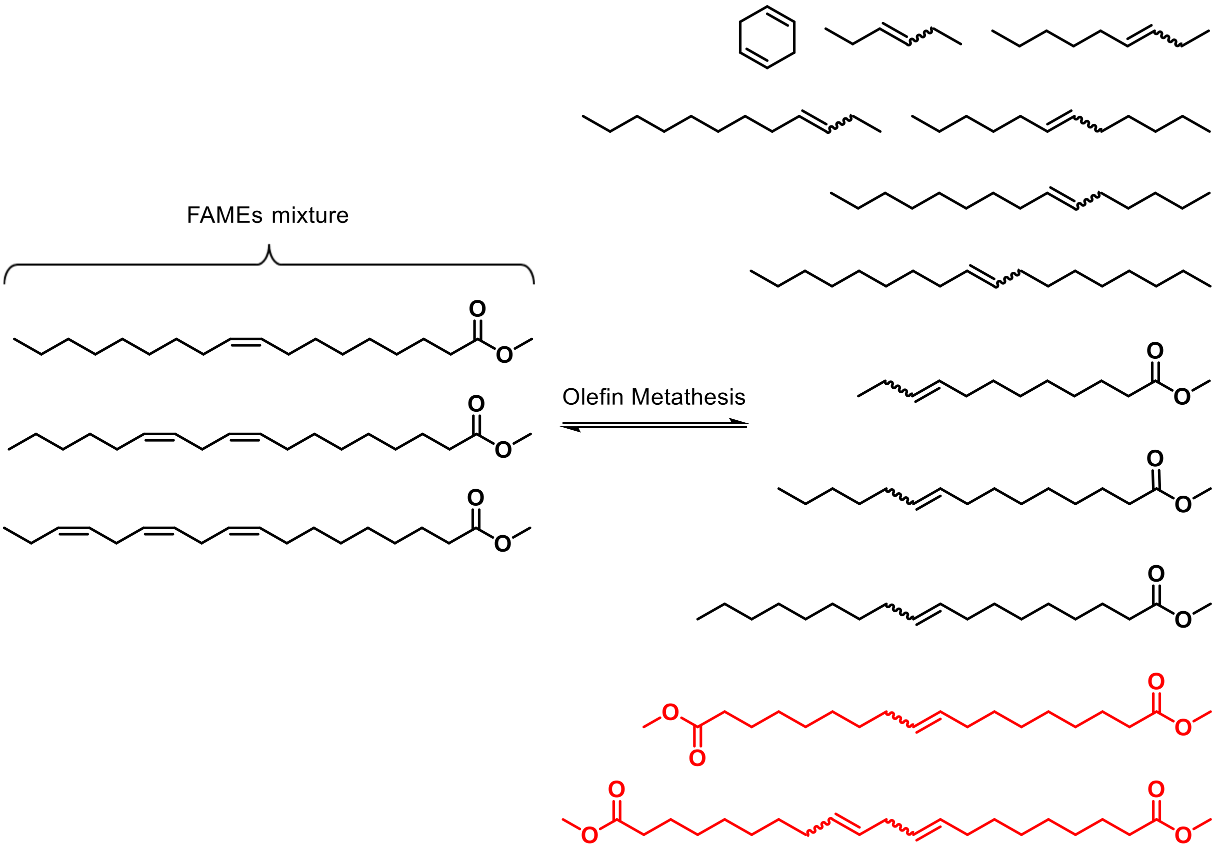
[a] Note that short-chain aliphatic polyesters, like poly lactide or poly(butylene succinate) feature substantial melting points > 100 ° C.

the authors themselves, this melting temperature is not that of a 'pure' polyester-18.18, as the monomer used is a mixture of the desired C_{18}-component (about 75 %) along with other isomers of different chain-length.



Scheme 3.6: Possible products from self-metathesis (and cross-metathesis) of FAME obtained from different plant oils.

Due to the fact that polyunsaturated triglycerides were applied as starting material a more complex product mixture, including polyenes, monoesters, diesters and cyclopolyenes was formed (**Scheme 3.6**). Thus after separation of the α,ω-difunctional compounds from the reaction mixture and subsequent hydrogenation of the double bond, Meier and coworkers, besides dimethyl-1,18-octadecanedioate, also obtained significant amounts of the corresponding C_{21}-diester. As a consequence the material prepared contains a mixture of repeat units of different carbon number (C_{18} and C_{21}). Such a less regular spacing of the ester groups could hinder the formation of sheets of ester groups and result in reduced order and melting points.[19,20,21] To this end, one can only note that our data are in-line with previous observations of other even carbon number long-chain polyesters-X,X (X = 20: T_m = 108 °C,[22] and X = 30: T_m = 113 ° C[16]).

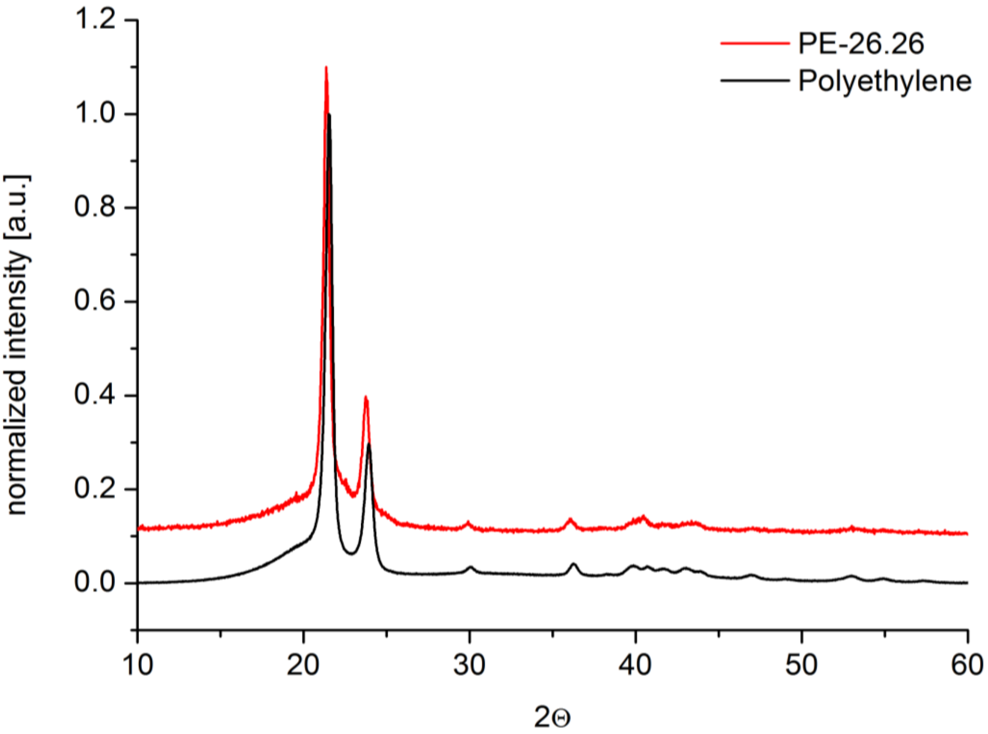
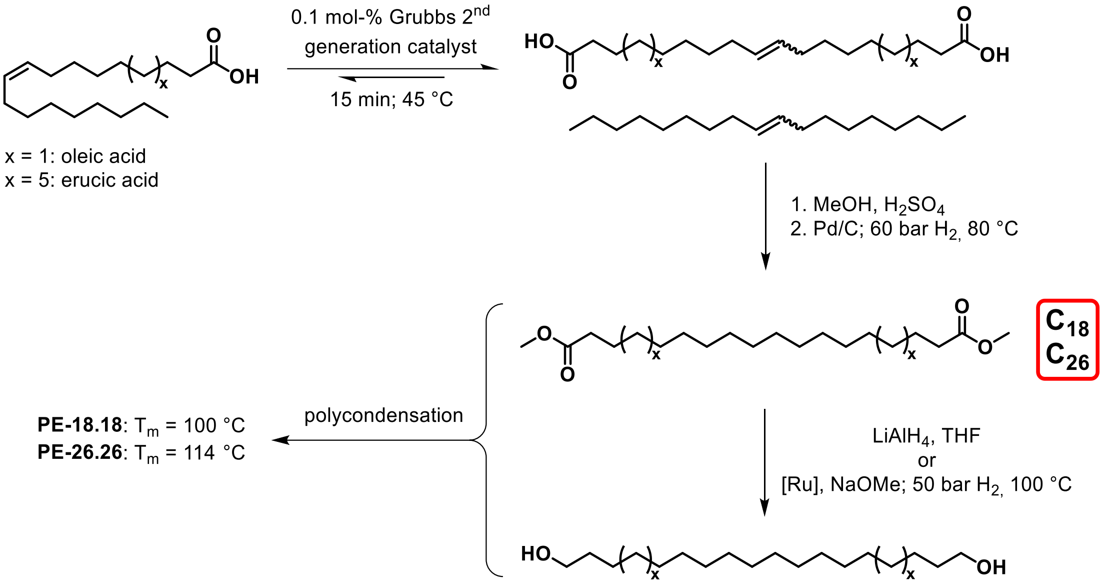


Figure 3.4: WAXD patterns of **PE-26.26** poly[1,26-hexacosanediyl-1,26-hexacosanedioate] (red) and linear polyethylene (black).

As observed for other long-chain aliphatic polyesters,[8] also for **PE-18.18** and **PE-26.26** orthorhombic, polyethylene-like crystal structures are found from WAXD measurements. Typical reflexes at 2Θ angles of 21.4° for the 110 plane and 23.8° for the 200 plane are measured (cf. **Figure 3.4** and **Figure 3.11**), illustrating the largely hydrocarbon character of these materials.

3.3 Conclusion

Self-metathesis of fatty acids from common plant oils applying [(PCy_3)(η-*C*-$C_3H_4N_2Mes_2$)-Cl_2Ru=CHPh] (Grubbs 2nd generation catalyst) followed by catalytic hydrogenation and purification via the ester, yields even numbered, long-chain aliphatic diesters. In this way, starting from technical grade oleic acid pure dimethyl-1,18-octadecanedioate was obtained. The even longer chain dimethyl-1,26-hexacosanedioate was prepared using erucic acid as a readily available fatty acid feedstock (**Scheme 3.7**).



Scheme 3.7: Approach for the synthesis of long-chain aliphatic diesters via self-metathesis of readily available fatty acid feedstocks.

Polyesterification with the corresponding diols, generated by reduction of the aforementioned diesters, stoichiometrically with $LiAlH_4$ or by catalytic hydrogenation with Saudan's[15] ruthenium catalyst, affords long-chain aliphatic polyesters, namely poly[1,18-octadecanediyl-1,18-octadecanedioate] (**PE-18.18**) and poly[1,26-hexacosanediyl-1,26-hexacosanedioate] (**PE-26.26**). **PE-26.26** features a melting-point of T_m = 114 °C (T_c = 92 °C, ΔH_m = 160 J g^{-1}), which is unsurpassed among the long-chain all-aliphatic polyesters reported to date (excluding model polymers with irregular spaced ester groups prepared in parallel to this work).[21,23]

3.4 Experimental section

3.4.1 Materials and general considerations

Unless stated otherwise, all manipulations were carried out under an inert gas atmosphere using standard Schlenk or glovebox techniques. THF and toluene were distilled from sodium under inert conditions. All other solvents were used in technical grade as received. Hydrogen (5.0) was supplied by Air Liquide. Technical grade erucic acid (≈ 90 %), $[(PCy_3)_2Cl_2Ru{=}CHPh]$ (Grubbs 1st generation catalyst), $[(PCy_3)(\eta\text{-}C\text{-}C_3H_4N_2Mes_2)Cl_2Ru{=}CHPh]$ (Grubbs 2nd generation catalyst), $[(PCy_3)_2Cl_2Ru{=}CH(^{i\text{-}Pr}O\text{-}C_6H_4)]$ (Hoveyda-Grubbs catalyst 1st generation), ethyl vinyl ether, lithium aluminum hydride, sodium methanolate and titanium(IV) butoxide (≥ 97 %) were supplied by Sigma Aldrich. Technical grade oleic acid (> 85 %) was purchased from TCI Europe. Palladium/charcoal activated (10 % Pd) was supplied by Merck. Dichlorobis[2-(diphenylphosphino)ethylamine]ruthenium was prepared by a literature procedure as reported previously[24] and 1,18-octadecanedioic acid (Emerox118®) was kindly donated by Emery Oleochemicals.

NMR spectra were recorded on a Varian Inova 400 and a Bruker Avance 400 spectrometer. ^1H and ^{13}C chemical shifts were referenced to the solvent signals. High-temperature NMR measurements of polymers were performed in 1,1,2,2-tetrachloroethane-*d2* at 130 °C.

GC analyses were carried out on a Perkin Elmer Clarus 500 GC system equipped with a Perkin Elmer Elite-5 capillary column (30 m × 0.25 mm × 0.25 µm, 5 % diphenyl - 95 % dimethyl polysiloxane) using flame-ionization detection (FID). Helium of 99.995 % purity was used as the carrier gas. The initial temperature of 100 °C was kept for one minute, and the column was then heated at a rate of 15 K min^{-1} to 300 °C, and kept isothermal at this temperature for 5 min (injector temperature 270 °C; detector temperature 280 °C).

GC-MS analyses were carried out on an Agilent Technologies 7890A GC system equipped with a Phenomenex Zebron ZB-5 ms w/Guardian capillary column (30m × 0.25 mm× 0.25 µm, 5 % phenyl - 95 % dimethyl polysiloxane) using mass (Agilent Technologies 5975C inert MSD with triple-axis detector) and flame-ionization detection (FID). Helium of 99.995 % purity was used as the carrier gas. The initial temperature of 50 °C was kept for 1 min, after which the column was heated at a rate of 30 °C min^{-1} up to 280 °C. The final temperature was kept for 8 min.

DSC analyses were performed on a Netzsch Phoenix 204 F1 instrument with a heating and cooling rate, respectively, of 10 K min^{-1}. Data reported are from second heating cycles.

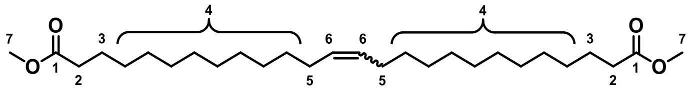
High temperature GPC measurements were carried out in 1,2,4-trichlorobenzene at 160 °C at a flow rate of 1 mL min^{-1} on a Polymer Laboratories 220 instrument equipped with Olexis columns with differential refractive index, viscosity, and light-scattering (15° and 90°) detectors. Data reported were determined directly against polyethylene standards.

3.4.2 Synthesis and characterization of Polyester-26.26 and Polyester-18.18

Synthesis of Dimethyl-1,26-hexacos-13-enedioate[6]

Erucic acid (45 g, 133.0 mmol) was weighed into a 250 mL glass reactor equipped with a mechanical stirrer. After heating to 45 °C, the melt was degassed several times and [(PCy$_3$)(η-C-C$_3$H$_4$N$_2$Mes$_2$)Cl$_2$Ru=CHPh] (Grubbs 2nd generation catalyst) (113 mg, 0.133 mmol) was added. The reaction mixture was stirred for 15 minutes at 45 °C. An off-white solid began to precipitate and the reaction was quenched with ethyl vinyl ether (10 mL). After addition of 100 mL of chloroform, the suspension was stirred for 30 minutes at 70 °C. The clear yellow solution was filtrated over celite and after removal of the solvent the crude diacid product was obtained by recrystallization from ethyl acetate.

For esterification the diacid was suspended in 150 mL of methanol. After addition of 8 drops of sulfuric acid, the resulting mixture was heated at 65 °C for half an hour. Pure dimethyl-1,26-hexacos-13-enedioate (14.9 g, 49 %) was obtained by repeated recrystallization from methanol.



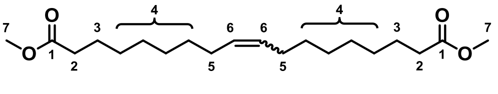
^{1}H NMR (CDCl$_3$, 25 °C, 400 MHz): δ 5.41-5.35 (m, 2H, H-6), 3.66 (s, 6H, H-7), 2.30 (t, $^3J_{H-H}$ = 7.4 Hz, 4H, H-2), 2.01-1.91 (m, 4H, H-5), 1.66-1.58 (m, 4H, H-3), 1.37-1.22 (m, 32H, H-4).

^{13}C{^{1}H} NMR (CDCl$_3$, 25 °C, 101 MHz): δ 174.47 (C-1), 130.49 (C-6), 51.55 (C-7), 34.26 (C-2), 32.75 (C-5), 30.08-29.00 (C-4), 25.11 (C-3).

Elemental analysis calculated for $C_{28}H_{52}O_4$: 74.29 % C, 11.58 % H; found: 74.54 % C, 11.34 % H.

Synthesis of Dimethyl-1,18-octadec-9-enedioate

Dimethyl-1,18-octadec-9-enedioate was prepared by self-metathesis of technical grade oleic acid according to the procedure described above for its longer chain analogue. After column chromatography on silica using pentane/EtOAc (8:1) as eluent, dimethyl-1,18-octadec-9-enedioate was obtained as white solid (6.5 g, 29 %).



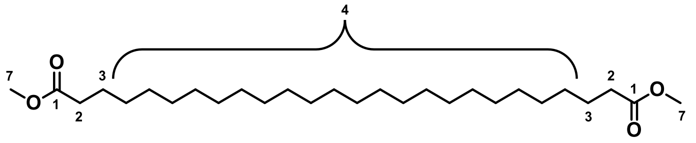
^{1}H NMR (CDCl$_3$, 25 °C, 400 MHz): δ 5.38-5.35 (m, 2H, H-6), 3.66 (s, 6H, H-7), 2.29 (t, $^3J_{H-H}$ = 7.6 Hz, 4H, H-2), 1.98-1.92 (m, 4H, H-5), 1.66-1.56 (m, 4H, H-3), 1.36-1.22 (m, 32H, H-4).

^{13}C{^{1}H} NMR (CDCl$_3$, 25 °C, 101 MHz): δ 174.43 (C-1), 130.45 (C-6), 51.56 (C-7), 34.25 (C-2), 32.68 (C-5), 29.91-28.90 (C-4), 25.09 (C-3).

Elemental analysis calculated for $C_{20}H_{36}O_4$: 70.55 % C, 10.66 % H; found: 70.75 % C, 11.54 % H

Synthesis of Dimethyl-1,26-hexacosanedioate

Dimethyl-1,26-hexacos-13-enedioate (14.9 g, 33.0 mmol) was dissolved in 90 mL of THF. After addition of 1.48 g Pd/C (10 % Pd), the reaction mixture was cannula transferred into a stirred pressure reactor and hydrogenated at 60 bar H_2 and 80 °C for 66 h. After cooling to room temperature, the reactor was vented. The reaction mixture was retrieved from the reactor and heated to around 50 °C to remove catalyst residues by filtration over celite. After removing the solvent *in vacuo* and recrystallization from methanol, dimethyl-1,26-hexacosanedioate (12.2 g, 82 %) was obtained in polymerization grade purity (≥ 99 %) as a white solid (cf. **Figure 3.3**).



^{1}H-NMR (CDCl$_3$, 25 °C, 400 MHz): δ 3.66 (s, 6H, H-7), 2.30 (t, $^3J_{H\text{-}H}$ = 7.4 Hz, 4H, H-2), 1.66-1.56 (m, 4H, H-3), 1.34-1.20 (m, 40H, H-4).

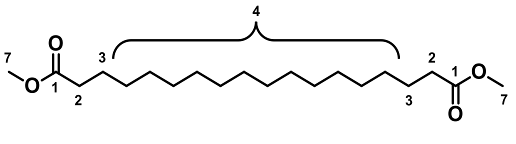
^{13}C{^{1}H} NMR (CDCl$_3$, 25 °C, 101 MHz): δ 174.49 (C-1), 51.57 (C-7), 34.27 (C-2), 30.23-29.02 (C-4), 25.12 (C-3).

Elemental analysis calculated for $C_{28}H_{54}O_4$: 73.96 % C, 11.37 % H; found: 74.14 % C, 12.56 % H.

Synthesis of Dimethyl-1,18-octadecanedioate

Dimethyl-1,18-octadecanedioate was prepared according to the procedure described above for its longer chain analogue. Recrystallization from methanol yielded the desired product (4.8 g, 80 %) in polymerization grade purity (≥ 99 %) as a white solid (cf. **Figure 3.5**).

Alternatively dimethyl-1,18-octadecanedioate can be prepared starting from octadecanedioic acid (Emerox 118®) by transesterification with methanol. For this purpose octadecanedioic acid (100.6 g, 0.32 mol) is suspended in 800 mL of methanol. After addition of 4 mL of sulfuric acid, the reaction mixture was heated at 70 °C for two hours. The resulting solution was then neutralized with aqueous Na_2CO_3 solution and extracted with diethyl ether (3 x 250 mL). The combined organic phases were washed with water (3 x 250 mL), brine (2 x 200 mL) and subsequently dried over $MgSO_4$. After removing the solvent *in vacuo* the desired product was obtained in polymerization grade purity (≥ 99 %) as a white solid (81.5 g, 74 %) by repeated recrystallization from methanol.



^{1}H-NMR (CDCl$_3$, 25 °C, 400 MHz): δ 3.66 (s, 6H, H-7), 2.30 (t, $^3J_{H\text{-}H}$ = 7.8 Hz, 4H, H-2), 1.66-1.56 (m, 4H, H-3), 1.34-1.20 (m, 24H, H-4).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C, 101 MHz): δ 174.47 (C-1), 51.57 (C-7), 34.27 (C-2), 29.89-29.21 (C-4), 25.12 (C-3).

Elemental analysis calculated for $C_{20}H_{38}O_4$: 70.13 % C, 11.18 % H; found: 70.24 % C, 11.60 % H

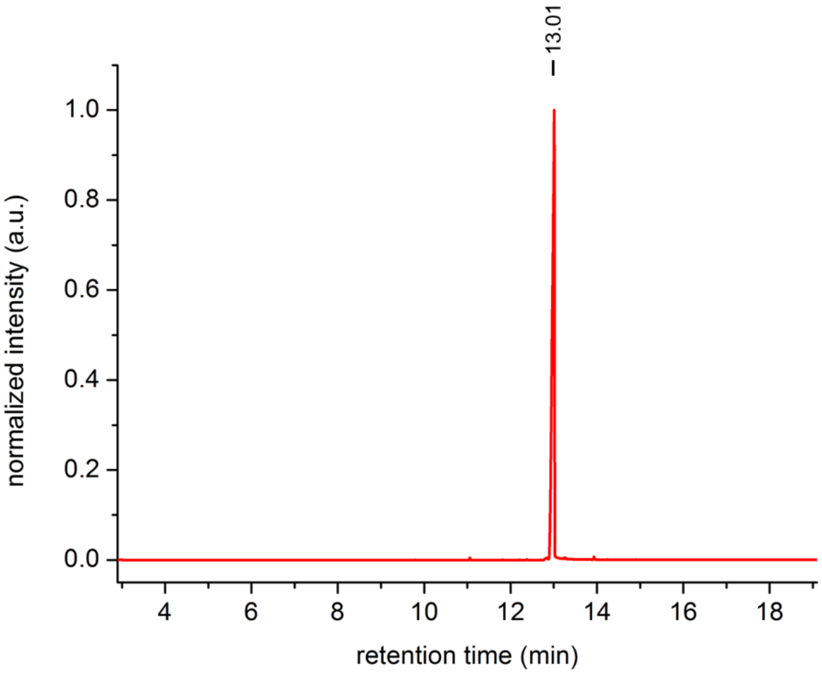
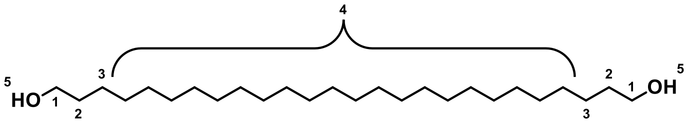


Figure 3.5: Gas chromatogram of pure dimethyl-1,18-octadecanedioate (≥ 99 % purity).

Synthesis of Hexacosane-1,26-diol

Dimethyl-1,26-hexacosanedioate (5.9 g, 13.0 mmol) was dissolved in 100 mL of THF. This solution was slowly added to a stirred and cooled suspension of $LiAlH_4$ (1.6 g; 42 mmol) in 40 mL of THF. After the addition, the reaction mixture was heated to reflux for 12 hours and then cooled to room temperature. The reaction was quenched by slow addition of 2.0 mL of water, 2.0 mL of 15 % aqueous NaOH and 6.0 mL of water. The reaction mixture was then filtrated at 50 °C over celite. After removing the solvent *in vacuo*, hexacosane-1,26-diol was recrystallized from chloroform to yield 4.4 g (85 %) of the pure product.



^{1}H-NMR ($CDCl_3$, 50 °C, 400 MHz): δ 3.64 (t, $^3J_{H\text{-}H}$ = 6.5 Hz, 4H, H-1), 1.61-1.53 (m, 4H, H-2), 1.41-1.24 (m, 44H, H-3 and H-4), 1.18 (br s, 2H, H-5).

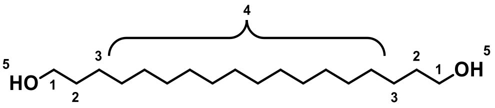
$^{13}C\{^1H\}$ NMR ($CDCl_3$, 50 °C, 101 MHz): δ 63.27 (C-1), 33.06 (C-2), 30.10-29.22 (C-4), 25.95 (C-3).

Elemental analysis calculated for $C_{26}H_{54}O_2$: 78.32 % C, 13.65 % H; found: 78.51 % C, 14.14 % H.

Synthesis of Octadecane-1,18-diol

The reduction of dimethyl-1,18-octadecanedioate was carried out analogously to the procedure described above for its 1,26-analogue. Octadecane-1,18-diol was recrystallized from chloroform to obtain 83 % yield (3.1 g).

Alternatively octadecane-1,18-diol can be obtained by catalytic reduction. This reaction was carried out, analogous to a reported procedure,[15] in a 300 mL stainless steel mechanically stirred pressure reactor equipped with a heating jacket and a glass inlay. Prior to the reduction experiment the reactor was purged several times with argon. Dimethyl-1,18-octadecanedioate (43.8 mmol; 15.0 g) was weighed under air into a dry Schlenk tube equipped with a magnetic stir bar which was then purged several times with argon. 120 mL of dry and degassed THF were added using standard Schlenk techniques. Vigorous stirring afforded a homogenous reaction mixture. In the glovebox dichlorobis[2-(diphenylphosphino)ethylamine]ruthenium (43.8 µmol; 28 mg) and sodium methanolate (2.20 mmol; 120 mg) were weighed into a second dry Schlenk tube equipped with a magnetic stir bar. After removing the Schlenk tube from the glovebox, 100 mL of dry and degassed THF were added. Both mixtures were then cannula-transferred into the reactor in an argon counter stream. The reactor was closed, pressurized with 50 bar hydrogen and then heated to 100 °C for 22 hours. After cooling down to room temperature the reactor was vented. The reaction mixture was retrieved from the reactor and heated to around 50 °C in order to remove catalyst residues by filtration over a Buchner funnel. Removing the solvent *in vacuo* and recrystallization from chloroform yielded octadecane-1,18-diol (11.2 g, 90 %).



^{1}H-NMR (CDCl$_3$, 25 °C, 400 MHz): δ 3.64 (t, $^3J_{H\text{-}H}$ = 6.5 Hz, 4H, H-1), 1.62-1.52 (m, 4H, H-2), 1.41-1.24 (m, 28H, H-3 and H-4), 1.13 (br s, 2H, H-5)

^{13}C{^{1}H} NMR (CDCl$_3$, 25 °C, 101 MHz): δ 63.26 (C-1), 33.06 (C-2), 30.20-29.32 (C-4), 25.96 (C-3).

Elemental analysis calculated for $C_{18}H_{38}O_2$: 75.46 % C, 13.37 % H; found: 75.17 % C, 13.70 % H

Synthesis of PE-26.26

Polyester-26,26 was prepared in a 100 mL two-necked Schlenk tube equipped with an overhead stirrer. Efficient mixing of the highly viscous polymer melt was achieved by a helical agitator. Under a static argon atmosphere the monomers (4.0 mmol of dimethyl-1,26-hexacosanedioate and 4.0 mmol of hexacosane-1,26-diol) were filled into the reaction vessel and molten by heating to 130 °C. Titanium(IV) butoxide (27 mg, 0.08 mmol) was injected, and the temperature was raised to 200 °C in the course of 7 hours. Subsequently the temperature was decreased to 180 °C and the polymer melt stirred for 19 h at this temperature under reduced pressure (0.01 mbar).

Poly[1,26-hexacosanediyl-1,26-hexacosanedioate] (10 K min^{-1}): T_m = 114 °C, T_c = 94 °C, and ΔH_m = 160 J g^{-1} (cf. **Figure 3.6**).

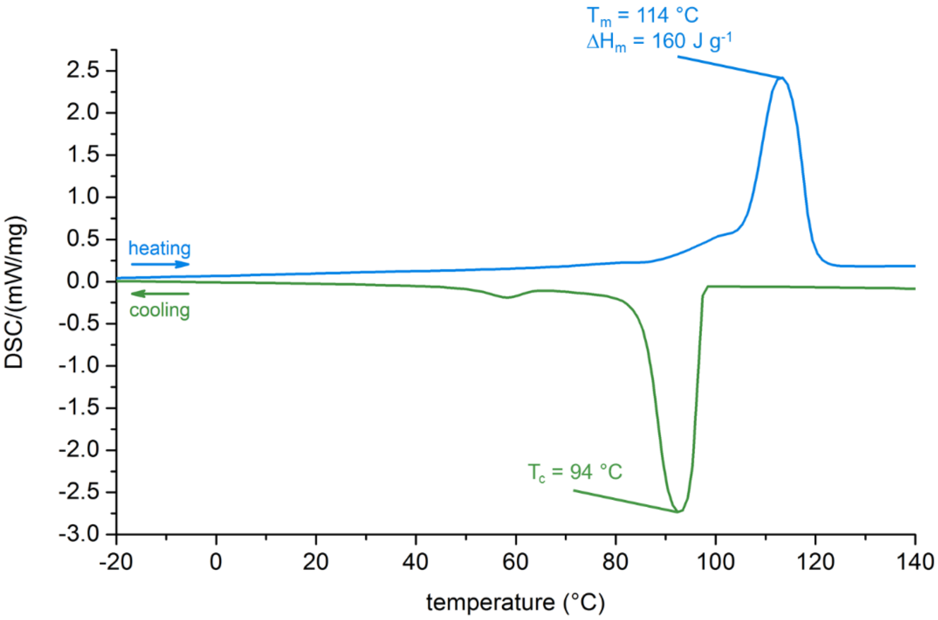
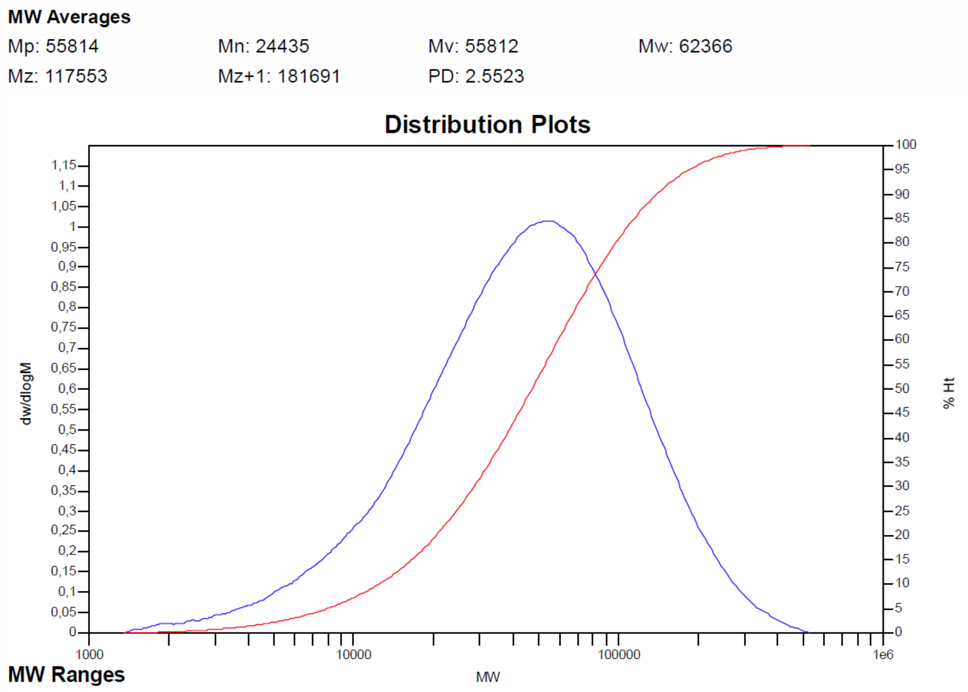


Figure 3.6: DSC trace of poly[1,26-hexacosanediyl-1,26-hexacosanedioate].

GPC reveals molecular weights M_n of typically 2.4 × 10^4 g mol^{-1} (M_w/M_n = 2.6) (cf. **Figure 3.7**); this data agrees with M_n of 2.0 × 10^4 g mol^{-1} determined from ^1H NMR spectroscopic analysis of the end groups (cf. **Chapter 3.4.3**).



MW Averages

Mp: 55814 Mn: 24435 Mv: 55812 Mw: 62366

Mz: 117553 Mz+1: 181691 PD: 2.5523

Figure 3.7: GPC trace of poly[1,26-hexacosanediyl-1,26-hexacosanedioate] (in 1,2,4-trichlorobenzene at 160 °C).

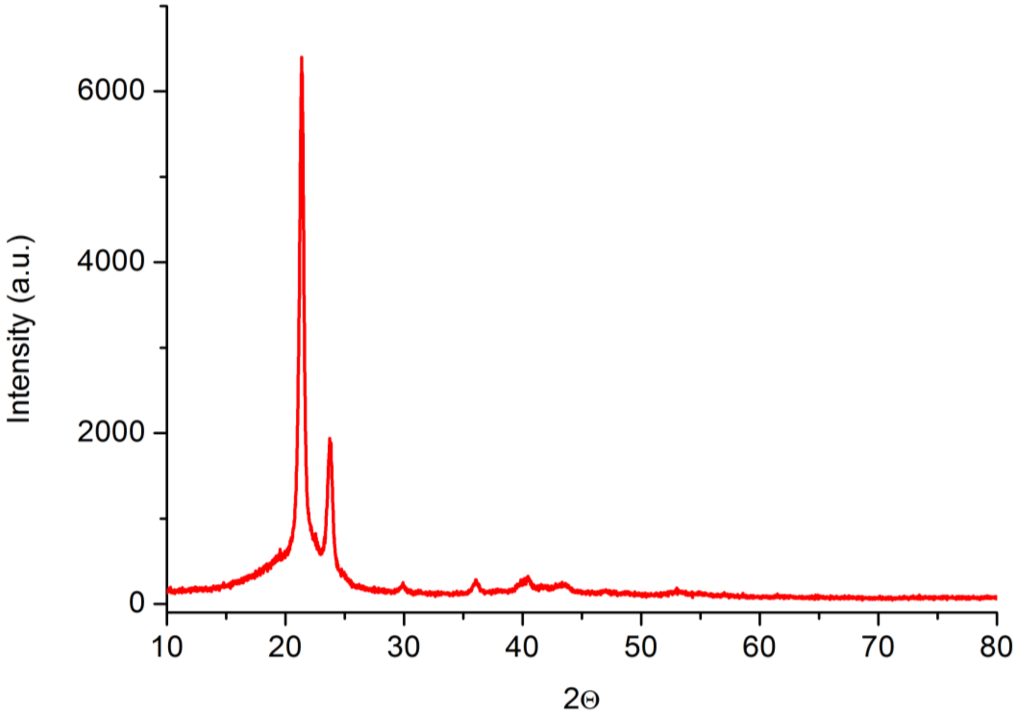


Figure 3.8: WAXD pattern of poly[1,26-hexacosanediyl-1,26-hexacosanedioate].

Synthesis of PE-18.18

Polyester-18.18 was prepared in a 100 mL two-necked Schlenk tube equipped with an overhead stirrer. Efficient mixing of the highly viscous polymer melt was achieved by a helical agitator. Under a static argon atmosphere the monomers (16.0 mmol of dimethyl-1,18-octadecanedioate and 16.0 mmol of octadecane-1,18-diol) were filled into the reaction vessel and molten by heating to 120 °C. Titanium(IV) butoxide (55 mg, 0.16 mmol) was added and the temperature was risen by 10 K every 45 minutes. At a temperature of 180 °C vacuum was applied to remove volatiles. Then the mixture was stirred overnight at 200 °C under reduced pressure (0.01 mbar).

Poly[1,18-octedecanediyl-1,18-octadecanedioate] (10 K min^{-1}): T_m = 100 °C, T_c = 77 °C, and ΔH_m = 153 J g^{-1} (cf. **Figure 3.9**).

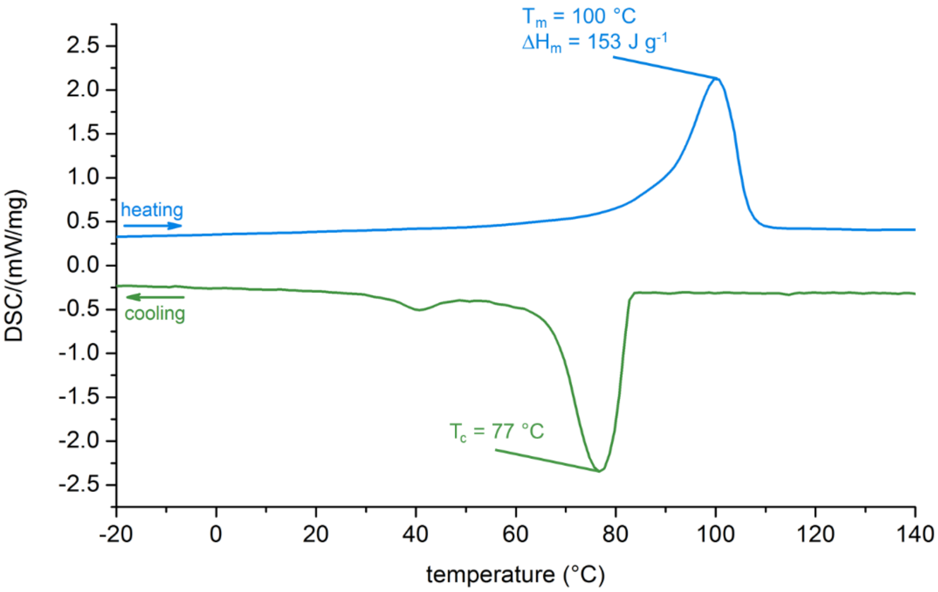
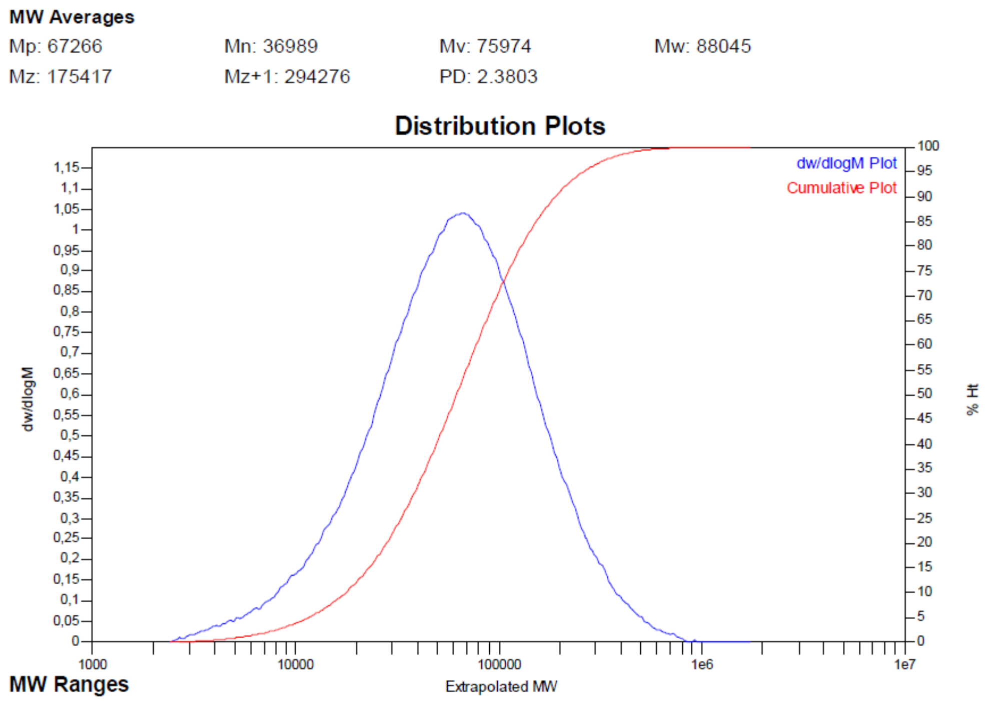


Figure 3.9: DSC trace of Poly[1,18-octedecanediyl-1,18-octadecanedioate]

GPC reveals molecular weights M_n of typically 3.7×10^4 g mol^{-1} (M_w/M_n = 2.4) (cf.); this data agrees with M_n of 3.2×10^4 g mol^{-1} determined from ^{1}H NMR spectroscopic analysis of the end groups (cf. **Chapter 3.4.3**).



MW Averages
Mp: 67266 Mn: 36989 Mv: 75974 Mw: 88045
Mz: 175417 Mz+1: 294276 PD: 2.3803

Figure 3.10: GPC trace of poly[1,18-octedecanediyl-1,18-octadecanedioate] (in 1,2,4-trichlorobenzene at 160 °C)

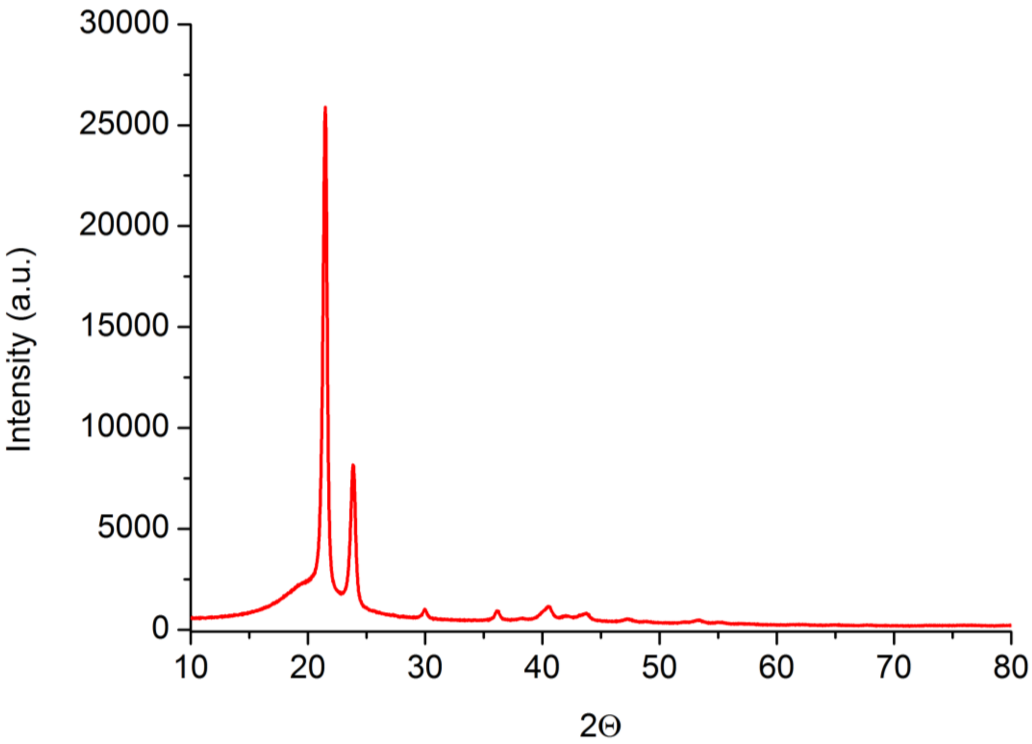


Figure 3.11: WAXD pattern of poly[1,18-octedecanediyl-1,18-octadecanedioate].

3.4.3 Molecular weight determination by ^{1}H-NMR spectroscopy

The molecular weight and the number-average degree of polymerization (DP_n) respectively, can be determined from signal intensities of endgroups compared to signals intensities of signals in proximity to the ester groups of the polymer chain in the ^{1}H-NMR spectra (**Figure 3.12**). Generally it is assumed that three different types of endgroups are present, here however only two endgroups can be seen:

- E_1: methyl ester endgroup (3.71 ppm, s, 3H)
- E_2: hydroxyl endgroup (3.67 ppm, t, 2H)
- E_3: butylester endgroup (0.96 ppm, t, 3H)

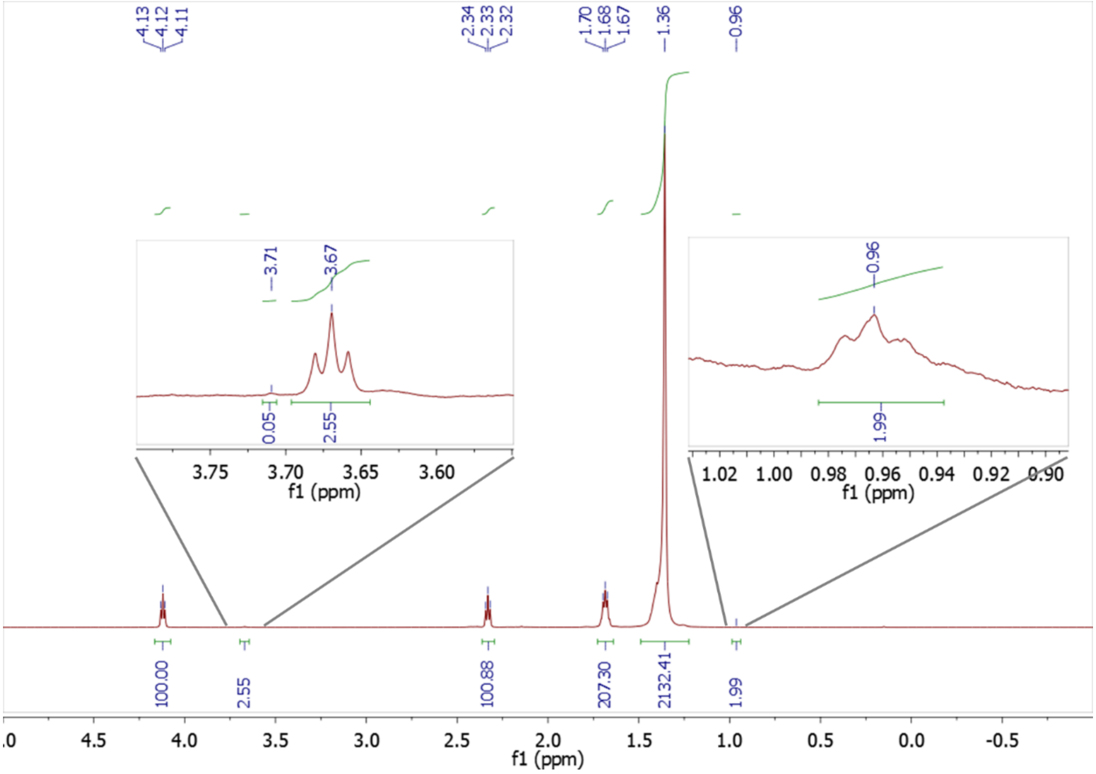


Figure 3.12: ^{1}H-NMR (600 MHz, $C_2D_2Cl_4$, 120°C) of poly[1,26-hexacosanediyl-1,26-hexacosanedioate]. Inserts show enlargement of the endgroup regions.

The number-average degree of polymerization (DP_n, defined here as the number of monomers incorporated, that is the number of X-$(CH_2)_y$-X, with X = COOH, CH_2OH) can be calculated from the integrals of these endgroups and for example the integral E_4 of the methylene group adjacent to the carbonyl group according to following equation:

$$DP_n = \frac{\int E_4}{\left({}^1\!/_3 E_1 + {}^1\!/_2 \int E_2 + {}^1\!/_3 \int E_3\right)} \approx 52$$

3.5 References

1. Metathesis of Unsaturated Fatty Acid Esters by a Homogeneous Tungsten Hexachloride-tetramethyltin Catalyst. Van Dam, P. B.; Mittelmeijer, M. C.; Boelhouwer, C. *J. Chem. Soc., Chem. Commun.* **1972**, *22*, 1221-1222.
2. a) Homogeneous Catalytic Metathesis of Unsaturated Fatty Esters: New Synthetic Method for Preparation of Unsaturated Mono- and Dicarboxylic Acids. Van Dam, P.; Mittelmeijer, M.; Boelhouwer, C. *J. Am. Oil Chem. Soc.* **1974**, *51*, 389-392. b) Heterogeneous Metathesis of Unsaturated Fatty Acid Esters. Verkuijlen, E.; Kapteijn, F.; Mol, J. C.; Boelhouwer, C. *J. Chem. Soc., Chem. Commun.* **1977**, *7*, 198-199.
3. Metathesis of Unsaturated Fatty Acid Esters and Fatty Oils. Mol, J. C. *J. Mol. Catal.* **1994**, *90*, 185-199.
4. The Development of L_2X_2RuCHR Olefin Metathesis Catalysts: An Organometallic Success Story. Trnka, T. M.; Grubbs, R. H. *Acc. Chem. Res.* **2000**, *34*, 18-29.
5. High Turnover Numbers with Ruthenium-Based Metathesis Catalysts. Dinger, M. B.; Mol, J. C. *Adv. Synth. Catal.* **2002**, *344*, 671-677.
6. a) Metathesis of Unsaturated Fatty Acids: Synthesis of Long-Chain Unsaturated-α,ω-Dicarboxylic Acids. Ngo, H.; Jones, K.; Foglia, T. *J. Am. Oil Chem. Soc.* **2006**, *83*, 629-634. b) Method of Producing Dicarboxylic Acids. Ngo, H.; Foglia, T. A. (United States Department of Agriculture) U.S. Patent 7,534,917 (B1), **2009**.
7. Search for New Industrial Oils. V.: Oils of Cruciferae. Mikolajczak, K. L.; Miwa, T. K.; Earle, F. R.; Wolff, I. A.; Jones, Q. *J. Am. Oil Chem. Soc.* **1961**, *38*, 678-681.
8. a) Linear Semicrystalline Polyesters from Fatty Acids by Complete Feedstock Molecule Utilization. Quinzler, D.; Mecking, S. *Angew. Chem. Int. Ed.* **2010**, *49*, 4306-4308. b) Long-Chain Linear C_{19} and C_{23} Monomers and Polycondensates from Unsaturated Fatty Acid Esters. Stempfle, F.; Quinzler, D.; Heckler, I.; Mecking, S. *Macromolecules* **2011**, *44*, 4159-4166.
9. Two-Step Biocatalytic Route to Biobased Functional Polyesters from ω-Carboxy Fatty Acids and Diols. Yang, Y.; Lu, W.; Zhang, X.; Xie, W.; Cai, M.; Gross, R. A. *Biomacromolecules* **2009**, *11*, 259-268.
10. Polyesters by Lipase-Catalyzed Polycondensation of Unsaturated and Epoxidized Long-Chain α,ω-Dicarboxylic Acid Methyl Esters with Diols. Warwel, S.; Demes, C.; Steinke, G. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 1601-1609.
11. a) Catalysis at the Interface of Ruthenium Carbene and Ruthenium Hydride Chemistry: Organometallic Aspects and Applications to Organic Synthesis. Schmidt, B. *Eur. J. Org.*

Chem. **2004**, *2004*, 1865-1880. b) Olefin Metathesis and Isomerization: From Undesired Side Reactions to Useful Synthetic Methodology. Schmidt, B. *J. Mol. Catal. A: Chem.* **2006**, *254*, 53-57.

12. a) Degradation of the First-Generation Grubbs Metathesis Catalyst with Primary Alcohols, Water, and Oxygen. Formation and Catalytic Activity of Ruthenium(II) Monocarbonyl Species. Dinger, M. B.; Mol, J. C. *Organometallics* **2003**, *22*, 1089-1095. b) Degradation of the Second-Generation Grubbs Metathesis Catalyst with Primary Alcohols and Oxygen - Isomerization and Hydrogenation Activities of Monocarbonyl Complexes. Dinger, M. B.; Mol, J. C. *Eur. J. Inorg. Chem.* **2003**, *2003*, 2827-2833. c) Decomposition of a Key Intermediate in Ruthenium-Catalyzed Olefin Metathesis Reactions. Hong, S. H.; Day, M. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **2004**, *126*, 7414-7415.
13. a) Prevention of Undesirable Isomerization during Olefin Metathesis. Hong, S. H.; Sanders, D. P.; Lee, C. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **2005**, *127*, 17160-17161. b) Tin and Iron Halogenides as Additives in Ruthenium-Catalyzed Olefin Metathesis. Meyer, W. H.; McConnell, A. E.; Forman, G. S.; Dwyer, C. L.; Kirk, M. M.; Ngidi, E. L.; Blignaut, A.; Saku, D.; Slawin, A. M. Z. *Inorg. Chim. Acta* **2006**, *359*, 2910-2917. c) Phenylphosphoric Acid as a New Additive to Inhibit Olefin Isomerisation in Ruthenium-Catalysed Metathesis Reactions. Gimeno, N.; Formentín, P.; Steinke, J. H. G.; Vilar, R. *Eur. J. Org. Chem.* **2007**, *2007*, 918-924.
14. a) Fermentative Herstellung der α,ω-Dicarbonsäure 1,18-Oktadecendisäure als Grundbaustein für Biobasierte Kunststoffe. Zibek, S.; Wagner, W.; Hirth, T.; Rupp, S.; Huf, S. *Chem. Ing. Tech.* **2009**, *81*, 1797-1808. b) Lipid Biotechnology: Industrially Relevant Production Processes. Schörken, U.; Kempers, P. *Eur. J. Lipid Sci. Technol.* **2009**, *111*, 627-645. c) Biotechnological Synthesis of Long-Chain Dicarboxylic Acids as Building Blocks for Polymers. Huf, S.; Krügener, S.; Hirth, T.; Rupp, S.; Zibek, S. *Eur. J. Lipid Sci. Technol.* **2011**, *113*, 548-561.
15. Dihydrogen Reduction of Carboxylic Esters to Alcohols under the Catalysis of Homogeneous Ruthenium Complexes: High Efficiency and Unprecedented Chemoselectivity. Saudan, L. A.; Saudan, C. M.; Debieux, C.; Wyss, P. *Angew. Chem. Int. Ed.* **2007**, *46*, 7473-7476.
16. Poly(triacontamethylene triacontanedioate) as Polyethylene Analogue: Properties and Enzymatic Degradation. Cho, I.; Lee, K. *Macromol. Chem. Phys.* **1997**, *198*, 861-869.
17. Plant Oil-Based Long-Chain C_{26} Monomers and Their Polymers. Vilela, C.; Silvestre, A. J. D.; Meier, M. A. R. *Macromol. Chem. Phys.* **2012**, *213*, 2220-2227.

18. Self-Metathesis of Fatty Acid Methyl Esters: Full Conversion by Choosing the Appropriate Plant Oil. Mutlu, H.; Hofsa; Montenegro, R. E.; Meier, M. A. R. *RSC Advances* **2013**, *3*, 4927-4934.
19. Encoding Crystal Microstructure and Chain Folding in the Chemical Structure of Synthetic Polymers. De Ten Hove, C. L. F.; Penelle, J.; Ivanov, D. A.; Jonas, A. M. *Nat. Mater.* **2004**, *3*, 33-37.
20. Characterization of Long-Chain Aliphatic Polyesters: Crystalline and Supramolecular Structure of PE22,4 Elucidated by X-ray Scattering and Nuclear Magnetic Resonance. Menges, M. G.; Penelle, J.; Le Fevere de Ten Hove, C.; Jonas, A. M.; Schmidt-Rohr, K. *Macromolecules* **2007**, *40*, 8714-8725.
21. From Polyethylene to Polyester: Influence of Ester Groups on the Physical Properties. Pepels, M. P. F.; Hansen, M. R.; Goossens, H.; Duchateau, R., *Macromolecules* **2013**, *46*, 7668-7677.
22. Aliphatic Long-Chain C_{20} Polyesters from Olefin Metathesis. Trzaskowski, J.; Quinzler, D.; Bährle, C.; Mecking, S. *Macromol. Rapid Commun.* **2011**, *32*, 1352-1356.
23. Long-Spaced Aliphatic Polyesters. Ortmann, P.; Mecking, S., *Macromolecules* **2013**, *46*, 7213-7218.

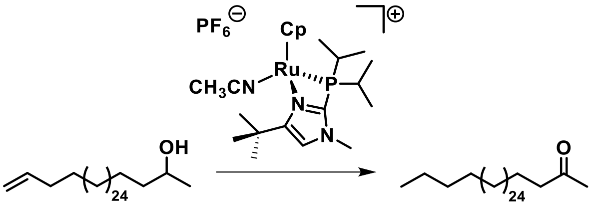
24 Hydrogenation of Esters with Ru/bidentate Ligands Complexes. Saudan, L.; Dupau, P.; Riedhauser, J.-J.; Wyss, P.; U.S. Patent 7,763,758 (B2), **2010**.

4 Unsymmetric AB-type polycondensation monomers via redox isomerization

4.1 Introduction

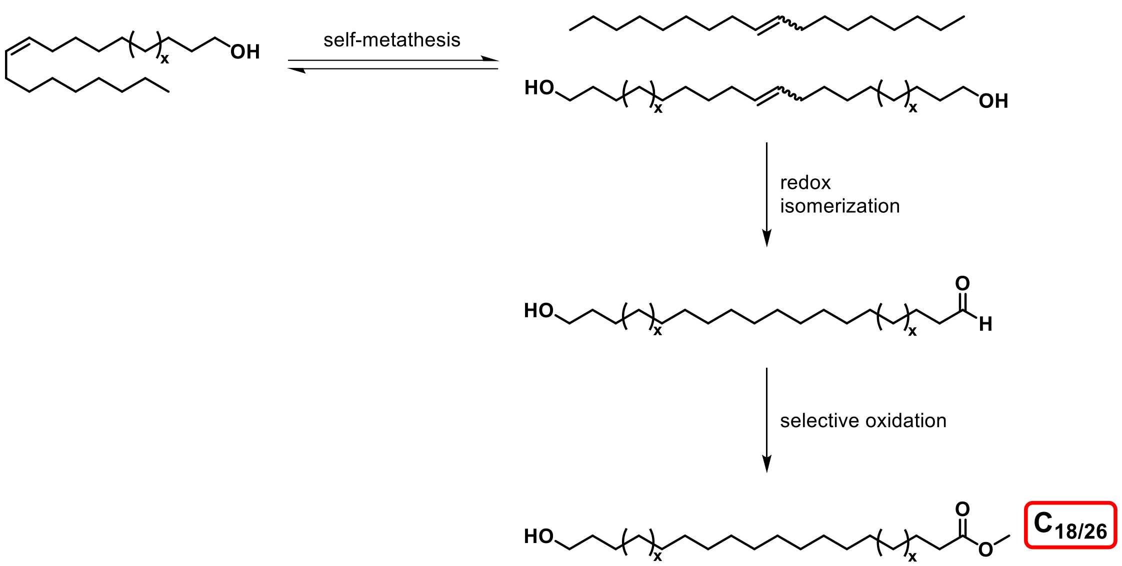
AB-type monomers are an alternative to the A_2+B_2 combinations discussed in the previous chapter. Potential advantages are the avoidance of monomer stoichiometry issues during polymerization. To date, long-chain AB-type monomers are accessible by multistep organic syntheses, or by biotechnological ω-hydroxylation, which is however limited in the chain length available. In this chapter, a route to unsymmetrical α,ω-functionalized long-chain compounds via olefin-metathesis combined with a redox isomerization is elaborated. Note that an isomerizing carbonylation route to unsymmetrical products was developed in parallel to this thesis in our group.[1]

Redox isomerizations represent an elegant and atom economical way to oxidize a specific site of an organic substrate.[2] The most common and well-studied example is the oxidation of allylic alcohols to aldehydes or ketones.[3,4] In these examples the double bond is moved over two positions. Redox isomerizations of more remote double bonds seem to be more challenging and only a few examples are reported so far. $Fe_3(CO)_{12}$ has been used successfully to convert 9-decen-1-ol to the corresponding saturated aldehyde.[5] However, a loading of 30 mol-% of the catalyst precursor, that is almost one metal center per alkenol, was required. In 2007 Grotjahn and coworkers presented the migration of alkene double bonds up to 30 positions employing a catalyst based on a cationic CpRu fragment and bifunctional imidazolylphosphine (**Scheme 4.1**).[6]



Scheme 4.1: Redox isomerization of the C_{32} alkenol dotriacont-31-en-2-ol.

Application of this reaction sequence to monounsaturated diols, obtained for example from self-metathesis of fatty alcohols, followed by selective oxidation of the aldehyde functionality should provide access to different ω-hydroxy carboxylic acid esters (**Scheme 4.2**).

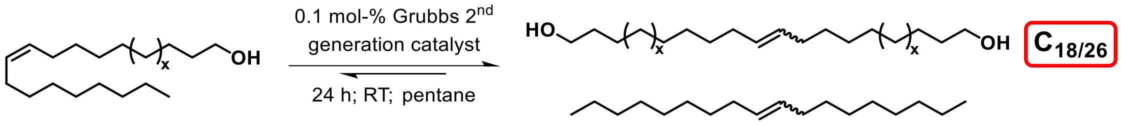


Scheme 4.2: Possible approach to linear, long-chain ω-hydroxy carboxylic acid esters.

4.2 Results and discussion

4.2.1 Synthesis of long-chain ω-hydroxy carboxylic acid esters of different chain-length

Self-metathesis of fatty alcohols under bulk conditions gives access to monounsaturated, bifunctional components.[7] However, due to the formation of side products and/or degradation of the catalyst,[8] conversion of the starting materials and yields of the corresponding diols are relatively low (≈ 20 %). This issue could be overcome by dissolving the fatty alcohol in pentane, as the desired products formed during the reaction were not soluble in the reaction medium and precipitated from the mixture. This removal of a product shifts the equilibrium of the reaction and therefore enhances conversion as well as the yield.



Scheme 4.3: Self-metathesis of oleyl- (x = 1) and erucyl-alcohol (x = 5).

In this way, starting from oleyl- and erucyl alcohol pure octadec-9-ene-1,18-diol and hexacos-13-ene-1,26-diol, respectively, could be obtained (**Scheme 4.3**). By contrast to this, self-metathesis of undec-10-en-1-ol under the same reaction conditions was accompanied by extensive double bond isomerization (**Figure 4.1**).

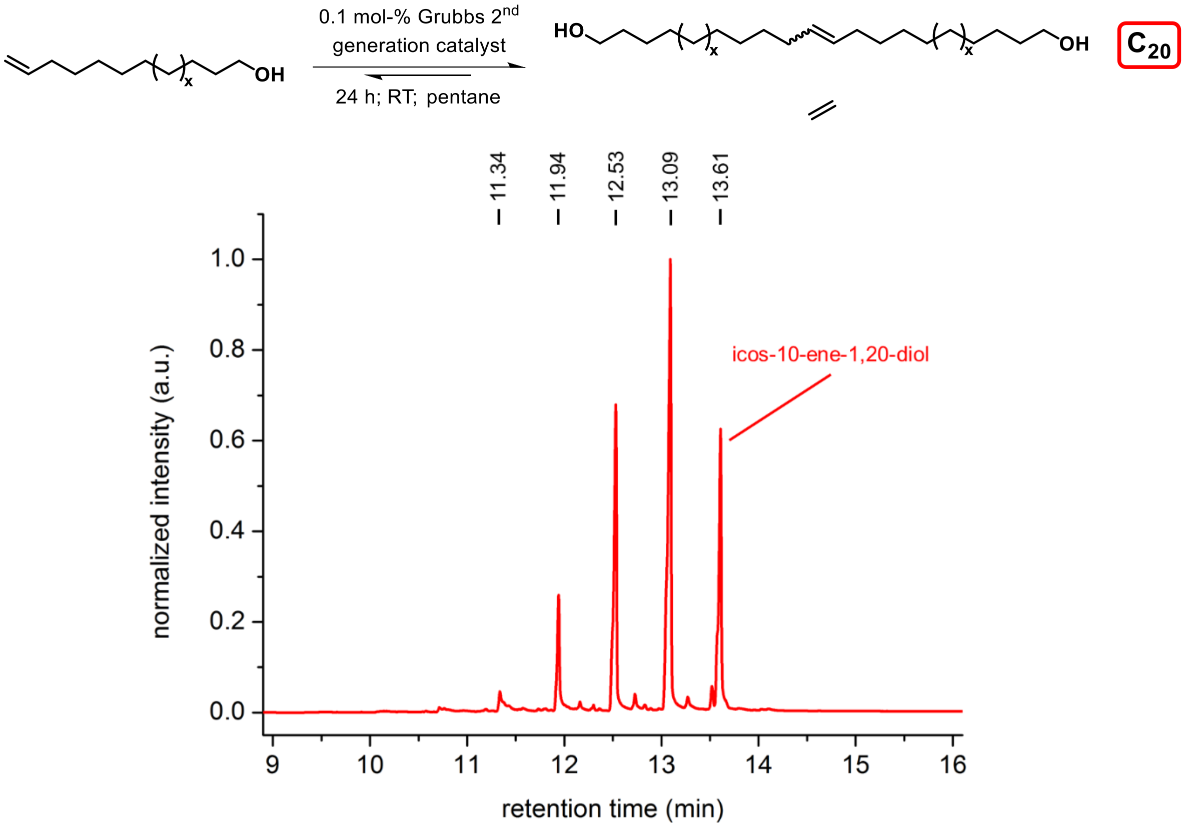


Figure 4.1: Gas chromatogram of the crude product from the self-metathesis of undec-10-en-1-ol.

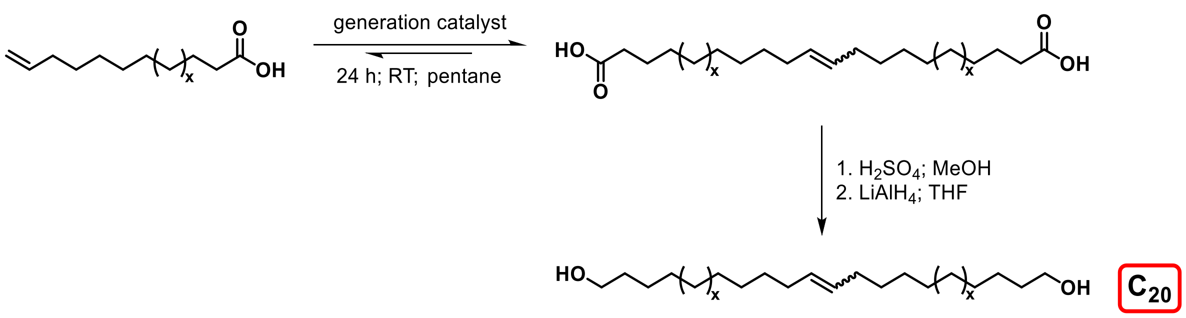
Besides the desired product eicos-10-ene-1,20-diol (t_r = 13.61 min), several other shorter-chain monounsaturated diols were formed. The compound with a retention time of t_r = 12.53 min for example could be identified as octadec-9-ene-1,18-diol. Yet, the pronounced tendency for isomerization, observed during self-metathesis of undec-10-en-1-ol, is not an issue in the metathetical transformations of internally unsaturated fatty alcohols described above. Consequently, the occurrence of this side-reaction might be attributed to the higher propensity for decomposition observed for the unsubstituted metal alkylidenes, [$L_nRu=CH_2$] formed during self-metathesis of terminal unsaturated compounds, compared to their substituted analogues, [$L_nRu=CHR$].[9] Moreover, internal alkenes in general are more stable and thus less reactive towards isomerization than terminal ones.[10] As a side note, also impurities that might be present in this particular substrate, such as traces of water, oxygen or peroxides, can contribute to the catalyst decomposition and thus further reinforce migration of the double bond.[11] However, neither reduction of the reaction time nor addition of *p*-benzoquinone could completely suppress this undesired side reaction in the metathetical transformation of undec-10-en-1-ol (**Table 4.1**).

Table 4.1: Self-metathesis of undec-10-en-1-ol applying different reaction times.[a]

entry	reaction time [h]	conversion[b] [%]	selectivity[b] [%]	isolated yield [%]
1	24	n.d.	23	42
2	5	n.d.	76	24
3	5[c]	n.d.	81	18

[a] Undec-10-en-1-ol (13 g, 75 mmol), Grubbs 2nd generation catalyst (64 mg, 0.075 mmol); 100 mL pentane; 25 °C. [b] Selectivity for the primary metathesis product eicos-10-ene-1,20-diol, determined by GC analysis of the crude reaction mixture.[c] addition of 1 mol-% *p*-benzoquinone.

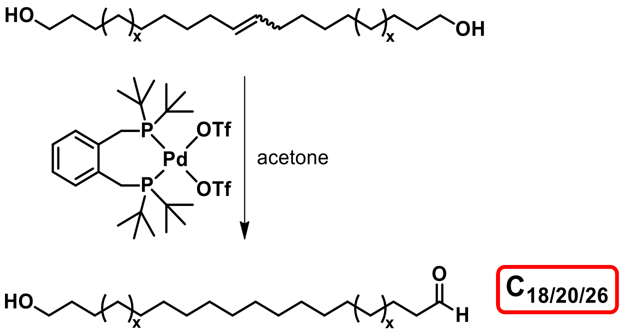
As isomerization is known to be suppressed in the presence of carboxylic acid groups,[12] eicos-10-ene-1,20-diol was synthesized by self-metathesis of undecenoic acid and subsequent reduction by means of $LiAlH_4$ (**Scheme 4.4**).[13]



Scheme 4.4: Synthesis of eicos-10-ene-1,20-diol by self-metathesis of undecenoic acid and subsequent reduction with $LiAlH_4$.

In this case $[(\mathrm{PCy}_3)_2\mathrm{CI}_2\mathrm{Ru{=}CHPh}]$ (Grubbs 1st generation catalyst) was applied. Albeit it is less reactive and less tolerant for polar and protic functionalities by comparison to its N-heterocycJic carbene analogue $[(\mathrm{PCy}_3)(\eta\text{-}C\text{-}\mathrm{C}_3\mathrm{H}_4\mathrm{N}_2\mathrm{Mes}_2)\mathrm{Cl}_2\mathrm{Ru{=}CHPh}]$ (Grubbs 2nd generation catalyst), it disfavors olefin isomerization.[14] Alternatively, pure eicos-10-ene-1,20-diol can be also prepared by self-metathesis of acetylated undec-10-en-1-ol, namely 10-undecenyl acetate, and subsequent removal of the corresponding protection group.[15]

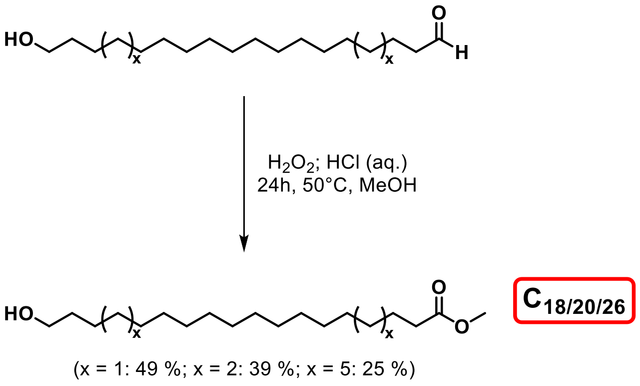
Redox isomerization of the monounsaturated diol components obtained in all these transformations give access to ω-hydroxy aldehydes of different chain-length (**Scheme 4.5**).



Scheme 4.5: Redox isomerization of monounsaturated diols.

Double bond migration was promoted by [1,2-bis{(di-*tert*-butylphosphino)methyl}benzene palladium ditriflate], which is known to be highly active for double bond isomerization even at low temperatures.[16] Stirring a suspension of the monounsaturated diol in acetone at room temperature for two hours in the presence of the Pd(II)-complex (1 mol-%) yielded the desired ω-hydroxy aldehyde. Conversions, as evidenced by ^{1}H NMR spectroscopy, typically decreased with increasing chain length of the monounsaturated diol, which might be attributed to the lower solubility of the starting material. For redox isomerization of octadec-9-ene-1,18-diol as well as eicos-10-ene-1,20-diol conversions of 73 % and 65 %, respectively were achieved, whereas for the redox isomerization of hexacos-13-ene-1,26-diol, applying the same reaction conditions, almost no conversion was observed. For the latter transformation even upon addition of further catalyst, increasing the reaction time up to 18 h and applying an elevated reaction temperature of 50 °C a conversion of only 52 % was obtained. In order to further improve the conversion of the unsaturated C_{26} diol increasing the solubility of the starting material by choosing an appropriate solvent might be helpful.

Oxidation of the aldehyde functionality to the corresponding ester was achieved by means of hydrogen peroxide and hydrochloric acid in methanol at 50 °C without isolation of the aldehyde intermediate (**Scheme 4.6**).[17] Non-optimized product yields due to the moderate conversions of the redox isomerization decreased from 49 % for methyl 18-hydroxyoctadecanoate to 25 % for methyl 26-hydroxyhexacosanoate. However, also in this reaction step the chain length of the starting material and along with that the lower solubility of the long-chain compound seem to have a negative influence on the overall product yield.



Scheme 4.6: Selective oxidation of the aldehyde functionality.

LC-MS analysis revealed that both the C_{18} as well as the C_{20} ω-hydroxy ester can be isolated in polymerization grade purity (≥ 99 %) by column chromatography and subsequent recrystallization from heptane (cf. **Figure 4.4** and **Figure 4.6**). By contrast to this, the ^{1}H-NMR spectra of the C_{26}-component still exhibits some minor impurities as evidenced for example by a singlet at 3.44 ppm, which might be attributed to the methoxy protons of the acetal group (**Figure 4.2**).

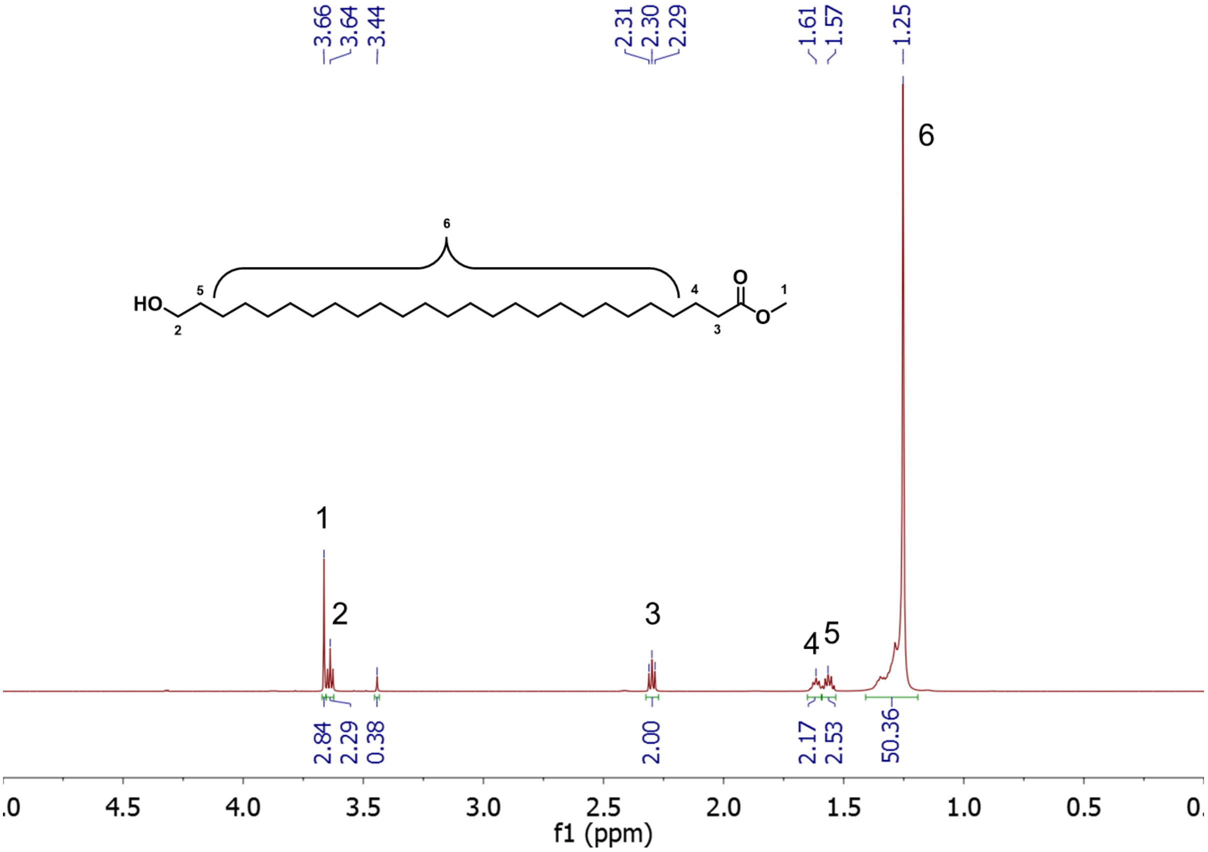


Figure 4.2: ^{1}H-NMR (400 MHz, $CDCl_3$, RT) of methyl 26-hydroxyhexacosanoate.

Complete separation of methyl 26-hydroxyhexacosanoate from this impurity could not be achieved, neither by recrystallization nor by column chromatography. For that reason only methyl 18-hydroxyoctadecanoate and methyl 20-hydroxyeicosanoate were utilized as starting materials for the synthesis of long-chain aliphatic polyesters.

4.2.2 Synthesis of Polyester-18 and Polyester-20

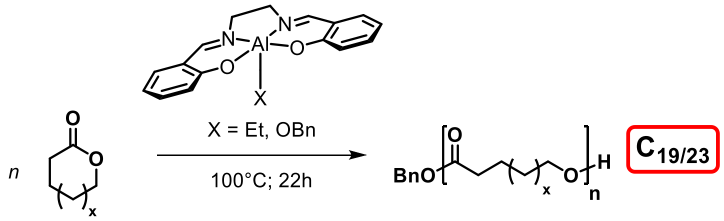
Polycondensation of these unsymmetrical AB-type monomers catalyzed by titanium alkoxides afforded the corresponding long-chain aliphatic polyesters, namely poly[ω-hydroxyl octadecanoic acid] (**PE-18**) and poly[ω-hydroxyl eicosanoic acid] (**PE-20**).

Table 4.2: Molecular weights and thermal properties of long-chain aliphatic AB-type polyesters.

entry	T_m[a] [°C]	T_c[a] [°C]	$M_{n,NMR}$[b] [g mol^{-1}]	$M_{n,GPC}$[c] [g mol^{-1}]	M_w/M_n[c]
PE-18	101	76	1.6×10^4	1.5×10^4	4.2
PE-20	103	84	1.5×10^4	1.3×10^4	2.9

a) Determined by DSC with a heating/cooling rate of 10 K min^{-1}. b) Determined by end-group analysis from ^{1}H-NMR spectroscopy. c) Determined by GPC at 160 °C in trichlorobenzene *vs.* polyethylene standards.

End-group analysis by ^{1}H-NMR spectroscopy, as well as high temperature GPC measurements relative to polyethylene standards, revealed number-average molecular weights in the order of several 10^4 g mol^{-1} (**Table 4.2**). As determined by DSC **PE-18** exhibits a melting point of T_m = 101 °C (T_c = 76 °C, ΔH_m = 143 J g^{-1}). For the even longer chain aliphatic polyester **PE-20** a melting point of T_m = 103 °C (T_c = 84 °C, ΔH_m = 166 J g^{-1}) was found. To this end one can only note that the melting temperature for **PE-18** is somewhat higher than the T_m of 90 °C reported for polyester-18 prepared by Narine and coworkers in parallel to this work.[18] Yet melting points reported here are in line with other long-chain AB-type polyesters such as **PE-19** (T_m = 103 °C) and **PE-23** (T_m = 104 °C) prepared by ring-opening polymerization of macrolactones (**Scheme 4.7**).[19]



Scheme 4.7: Ring-opening polymerization of poly(nonadecalactone) (x = 15) and poly(tricosalactone) (x = 19).[19]

4.3 Conclusion

In summary, linear long-chain ω-hydroxy aldehydes of different chain-lengths can be prepared by redox isomerization of monounsaturated diols, obtained from self-metathesis of fatty alcohols. Alternatively, these unsaturated diols can be obtained by reduction of the corresponding dicarboxylic acids, which are a (side-) product from olefin-metathesis of plant oils.

Double bond migration at room-temperature is promoted by the well-defined catalyst precursor [1,2-bis{(di-*tert*-butylphosphino)methyl}benzene palladium ditriflate]. Subsequent selective oxidation of the aldehyde functionality of these unsymmetrical α,ω-functionalized long-chain compounds gives access to different ω-hydroxy carboxylic acid esters, which are typically difficult and expensive to prepare by traditional organic syntheses. In this way, starting from commonly available plant oil derivatives, methyl 18-hydroxyoctadecanoate and methyl 20-hydroxyeicosanoate were obtained in polymerization grade purity (cf. **Scheme 4.2**). Their even longer chain analogue namely methyl 26-hydroxyhexacosanoate, however, still contained some minor unidentified impurities.

Polycondensation of these unsymmetrical AB-type monomers yielded long-chain aliphatic polyesters, namely poly[ω-hydroxyl octadecanoic acid] (**PE-18**) and poly[ω-hydroxyl eicosanoic acid] (**PE-20**). Molecular weights as determined by end-group analysis by ^{1}H-NMR spectroscopy, as well as high temperature GPC measurements, revealed number-average molecular weights on the order of several 10^4 g mol^{-1}. Thermal analysis exhibited a melting point of T_m = 101 °C (T_c = 76 °C, ΔH_m = 143 J g^{-1}) for **PE-18**, whereas for the even longer chain aliphatic polyester **PE-20** a melting point of T_m = 103 °C (T_c = 84 °C, ΔH_m = 166 J g^{-1}) was found. Thus melting points of these new polycondensates are significantly higher than for common mid-chain aliphatic polyesters and are in line with other long-chain AB-type polyesters reported so far.

4.4 Experimental section

4.4.1 Materials and general considerations

Unless stated otherwise, all manipulations were carried out under an inert gas atmosphere using standard Schlenk or glovebox techniques. THF and toluene were distilled from sodium under inert conditions. All other solvents were used in technical grade as received. Technical grade erucic acid (≈ 90 %), oleyl alcohol (85 %), 10-undecenoic acid (98 %), $[(PCy_3)_2Cl_2Ru{=}CHPh]$ (Grubbs 1st generation catalyst), $[(PCy_3)(\eta\text{-}C\text{-}C_3H_4N_2Mes_2)Cl_2Ru{=}CHPh]$ (Grubbs 2nd generation catalyst), ethyl vinyl ether, lithium aluminum hydride, titanium(IV) butoxide (≥ 97 %) were supplied by Sigma Aldrich. $[Pd(dtbpx)(OTf)_2]$ was prepared as reported previously.[20] Aqueous H_2O_2 (30 wt.-%) was purchased from Merck. All deuterated solvents were supplied by Eurisotop.

NMR spectra were recorded on a Varian Inova 400 and a Bruker Avance 400 spectrometer. ^1H and ^{13}C chemical shifts were referenced to the solvent signals. High-temperature NMR measurements of polymers were performed in 1,1,2,2-tetrachloroethane-*d2* at 130 °C.

GC analyses were carried out on a Perkin Elmer Clarus 500 GC system equipped with a Perkin Elmer Elite-5 capillary column (30 m × 0.25 mm × 0.25 μm, 5 % diphenyl - 95 % dimethyl polysiloxane) using flame-ionization detection (FID). Helium of 99.995 % purity was used as the carrier gas. The initial temperature of 100 °C was kept for one minute, and the column was then heated at a rate of 15 K min^{-1} to 300 °C, and kept isothermal at this temperature for 5 min (injector temperature 270 °C; detector temperature 280 °C).

GC-MS analyses were carried out on an Agilent Technologies 7890A GC system equipped with a Phenomenex Zebron ZB-5 ms w/Guardian capillary column (30m × 0.25 mm× 0.25 μm, 5 % phenyl - 95 % dimethyl polysiloxane) using mass (Agilent Technologies 5975C inert MSD with triple-axis detector) and flame-ionization detection (FID). Helium of 99.995 % purity was used as the carrier gas. The initial temperature of 50 °C was kept for 1 min, after which the column was heated at a rate of 30 °C min^{-1} up to 280 °C. The final temperature was kept for 8 min.

DSC analyses were performed on a Netzsch Phoenix 204 F1 instrument with a heating and cooling rate, respectively, of 10 K min^{-1}. Data reported are from second heating cycles.

High temperature GPC measurements were carried out in 1,2,4-trichlorobenzene at 160 °C at a flow rate of 1 mL min^{-1} on a Polymer Laboratories 220 instrument equipped with Olexis columns with differential refractive index, viscosity, and light-scattering (15° and 90°) detectors. Data reported were determined directly against polyethylene standards.

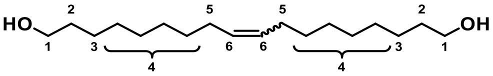
LC-MS analyses were conducted on a LCMS-2020 instrument from Shimadzu (pumps LC-20 AD, autosampler SIL-20AT HAT, column oven CTO-20AC, UV-Vis detector SPD-20A, controller CBM-20, APCI detector and software LCMS-solution) with an EC 125/4 Nucleodur

C18, 3 µM column (Machery-Nagel). A binary gradient of acetonitrile (with 0.1 % formic acid) in water (with 0.1 % formic acid) was used at a flow rate of 0.4 mL min^{-1}. Analytical high performance liquid chromatography (HPLC) was conducted on a Shimadzu LC-20A prominence system (pumps LC-20AT, auto sampler SIL-20A, column oven CTO-20AC, diode array detector SPD-M20A, ELSD-LT II detector, controller CBM-20A and software LC-solution) using an EC 125/4 Nucleodur C18, 3 µM column (Machery-Nagel).

4.4.2 Monomer synthesis

Synthesis of Octadec-9-ene-1,18-diol

Degassed oleyl alcohol (20.1 g, 75.0 mmol) was placed in 100 mL of pentane and [(PCy$_3$)(η-C-C$_3$H$_4$N$_2$Mes$_2$)Cl$_2$Ru=CHPh] (Grubbs 2nd generation catalyst) (64 mg, 0.075 mmol) was added. The reaction mixture was stirred over night at room temperature and quenched with ethyl vinyl ether (10 mL). After addition of 50 mL of pentane the reaction mixture was cooled to 5 °C and an off-white solid was filtered off. Repeated recrystallization from acetone yielded pure octadec-9-ene-1,18-diol (6.5 g, 60 %)



^{1}H-NMR (CDCl$_3$, 25 °C, 400 MHz): δ 5.41-5.29 (m, 2H, H-6), 3.63 (t, $^3J_{H\text{-}H}$ = 6.6 Hz, 4H, H-1), 2.00-1.92 (m, 4H, H-5), 1.61-1.52 (m, 4H, H-2), 1.43-1.23 (m, 20H, H-3 and H-4).

^{13}C{^{1}H} NMR (CDCl$_3$, 25 °C, 101 MHz): δ 130.51 (C-6), 63.22 (C-1), 32.94 (C-2), 32.71 (C-5), 29.84-29.10 (C-4), 25.87 (C-3).

Elemental analysis calculated for $C_{18}H_{36}O_2$: 76.00 % C, 12.76 % H; found: 76.11 % C, 12.69 % H.

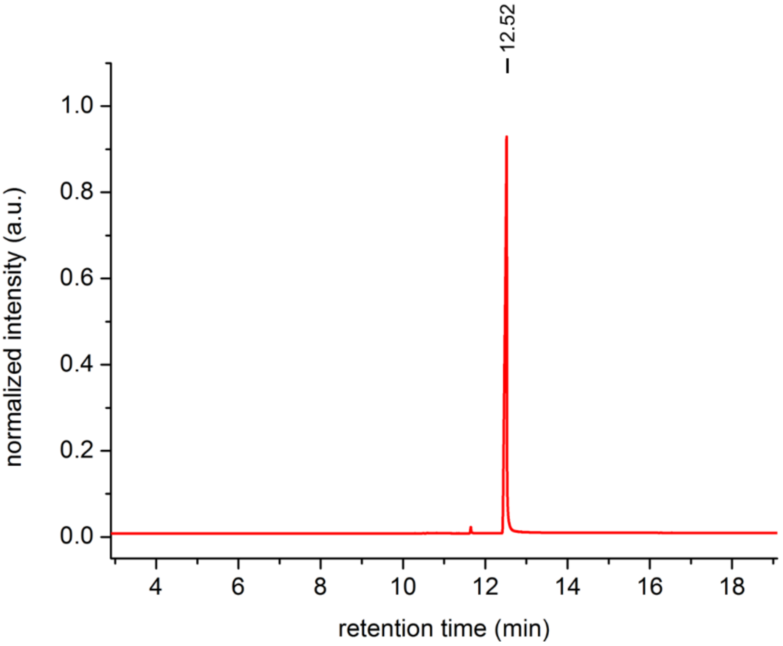
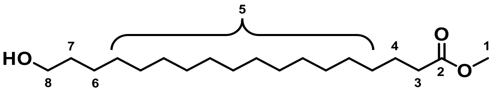


Figure 4.3: Gas chromatogram of pure octadec-9-ene-1,18-diol.

Synthesis of Methyl 18-hydroxyoctadecanoate

Octadec-9-ene-1,18-diol (4.8 g, 17.0 mmol) was suspended in 100 mL of acetone and [Pd(dtbpx)(OTf)$_2$] (135.8 mg, 0.17 mmol) was added. The reaction mixture was stirred for two hours at room temperature and the solvent was removed *in vacuo*. The crude product was suspended in 100 mL of methanol and 2.5 mL of concentrated HCl (≥ 37 %) were added dropwise at 4 °C. During the addition, the internal temperature was kept below 20 °C. After stirring with ice-cooling for 30 minutes, 3.1 mL aqueous H_2O_2 (30 wt.-%) were added and the reaction mixture was stirred for one hour. The mixture was heated to 50 °C and stirred over night at this temperature. The reaction mixture was then diluted with water and extracted with ethyl acetate (3 x 100 mL). The combined organic phases were washed with aqueous Na_2SO_3 (2 x 50 mL) and dried over $MgSO_4$. After filtration and removal of the solvent, the crude product was purified by column chromatography over silica using CH_2Cl_2/EtOAc (9:1) as eluent. Recrystallization from heptane yielded the desired product was as a white solid (2.6 g, 49 %).



^{1}H-NMR ($CDCl_3$, 25 °C, 600 MHz): δ 3.66 (s, 3H, H-1), 3.64 (t, $^3J_{H\text{-}H}$ = 6.7 Hz, 2H, H-8), 2.30 (t, $^3J_{H\text{-}H}$ = 7.7 Hz, 2H, H-3), 1.64-1.59 (m, 4H, H-4), 1.59-1.54 (m, 4H, H-7), 1.40-1.23 (m, 26H, H-5 and H-6).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C, 151 MHz): δ 174.50 (C-2), 63.25 (C-8), 51.59 (C-1), 34.29 (C-3), 32.98 (C-7), 29.94-29.19 (C-5), 25.90 (C-6), 25.13 (C-4).

Elemental analysis calculated for $C_{19}H_{38}O_3$: 72.56 % C, 12.18 % H; found: 72.34 % C, 12.93 % H.

APCI-MS: m/z = 356.1 (M^+ + H + MeCN).

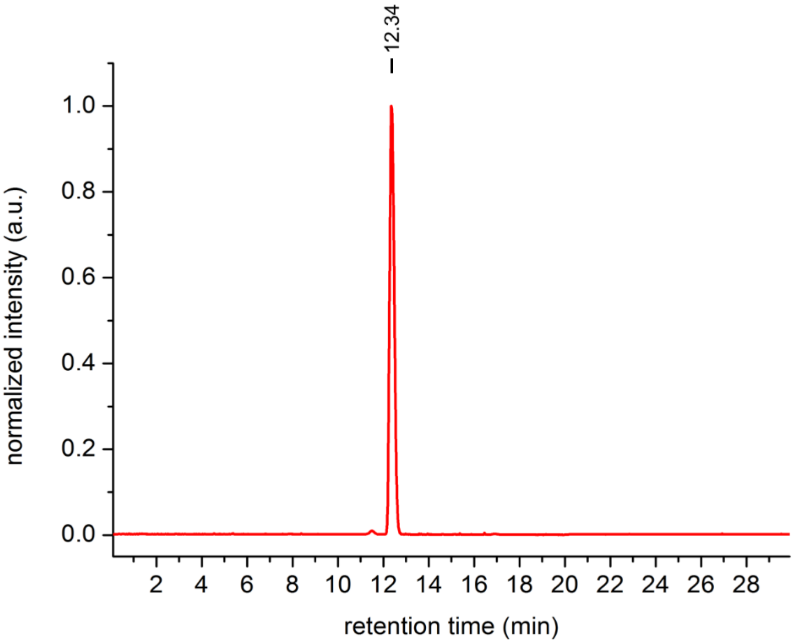
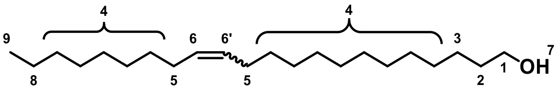


Figure 4.4: LC-MS chromatogramm of methyl 18-hydroxyoctadecanoate.

Synthesis of Erucyl Alcohol (Docos-13-en-1-ol)

Erucic acid (30.0 g, 88.6 mmol) was dissolved in 100 mL of THF and added dropwise to a cooled suspension (0 °C) of $LiAlH_4$ (5.0 g, 132.5 mmol) in 150 mL of THF. After complete addition, the suspension was refluxed for 3 h and then stirred overnight at room temperature. The reaction was quenched by slow addition of 5.5 mL of water, 5.5 mL of 2 M NaOH and 10.0 mL of water. The resulting solution was extracted with diethyl ether (3 x 100 mL). The combined organic phases were washed with water (2 x 150 mL), brine (2 x 100 mL) and subsequently dried over $MgSO_4$. After filtration, the solvent was removed *in vacuo* yielding 27.8 g (97 %) of the crude product as a white solid, which was utilized without further purification.

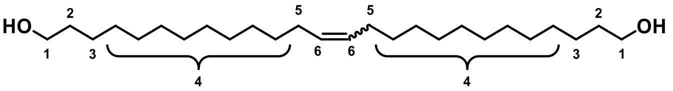


^{1}H NMR ($CDCl_3$, 25 °C, 400 MHz): δ 5.43-5.31 (m, 2H, H-6), 3.66 (t, $^3J_{H\text{-}H}$ = 6.7 Hz, 2H, H-1), 2.09-1.95 (m, 4H, H-5), 1.62-1.52 (m, 2H, H-2), 1.42-1.22 (m, 30H, H-3 and H-4).

^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C, 101 MHz): δ 130.52 and 130.50 (C-6, C-6'; *trans*), δ 130.05 and 130.03 (C-6, C-6'; *cis*), 63.23 (C-1), 32.97 (C-2), 32.06 (C-7), 30.05-29.26 (C-4), 27.35 (C-5), 25.88 (C-3), 22.83 (C-8), 14.26 (C-9).

Synthesis of Hexacos-13-ene-1,26-diol

After erucyl alcohol (27.5 g, 85.5 mmol) was degassed 100 mL of pentane and [$(PCy_3)(\eta$-C-$C_3H_4N_2Mes_2)Cl_2Ru$=CHPh] (Grubbs 2nd generation catalyst) (72 mg, 0.085 mmol) was added. The reaction mixture was stirred over night at room temperature and quenched with ethyl vinyl ether (10 mL). After addition of 50 mL of pentane the reaction mixture was cooled to 5 °C and an off-white solid was filtered off. Repeated recrystallization from acetone yielded pure hexacos-13-ene-1,26-diol (7.8 g, 46 %).



^{1}H-NMR ($CDCl_3$, 25 °C, 400 MHz): δ 5.41-5.29 (m, 2H, H-6), 3.64 (t, $^3J_{H\text{-}H}$ = 6.5 Hz, 4H, H-1), 1.99-1.92 (m, 4H, H-5), 1.61-1.52 (m, 4H, H-2), 1.38-1.21 (m, 36H, H-3 and H-4).

^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C, 101 MHz): δ 130.52 (C-6), 63.26 (C-1), 32.98 (C-2), 32.76 (C-5), 29.91-29.06 (C-4), 25.90 (C-3).

Elemental analysis calculated for $C_{26}H_{52}O_2$: 78.72 % C, 13.21 % H; found: 78.94 % C, 13.47 % H.

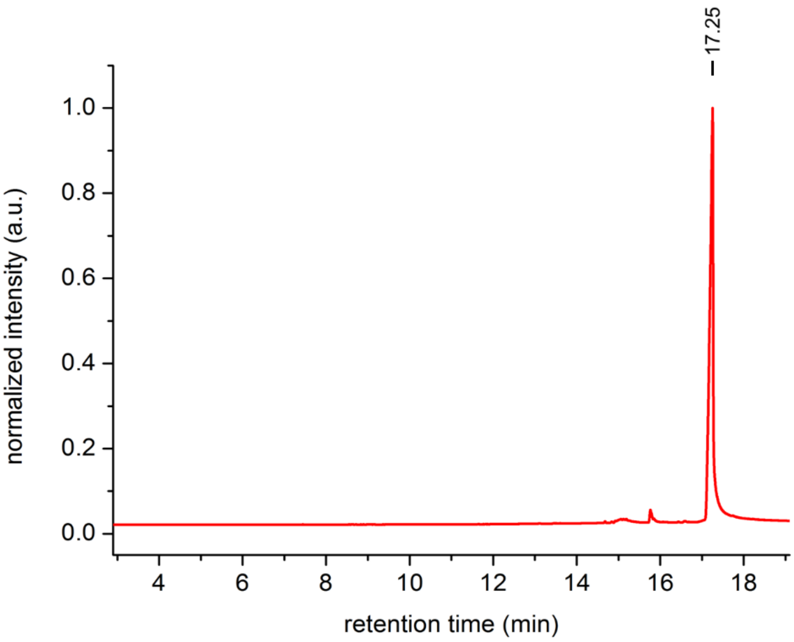
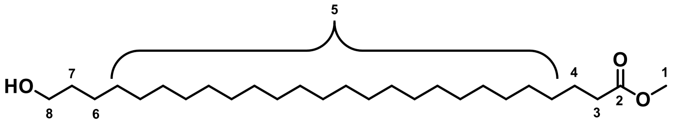


Figure 4.5: Gas chromatogram of pure hexacos-13-ene-1,26-diol.

Synthesis of Methyl 26-hydroxyhexacosanoate

Hexacos-13-ene-1,26-diol (6.7 g, 17.0 mmol) was suspended in 100 mL of acetone and [Pd(dtbpx)(OTf)$_2$] (135.8 mg, 0.17 mmol) was added. The reaction mixture was stirred for six hours at room temperature and the solvent was removed *in vacuo*. Due to the low conversion as evidenced by ^{1}H-NMR spectroscopy additional catalyst (60.0 mg, 0.08 mmol) and 100 mL of acetone were added and the suspension was stirred overnight at 50 °C. The crude product was suspended in 60 mL of methanol and 2.5 mL of concentrated HCl (≥ 37 %) were added dropwise at 4 °C. During the addition, the internal temperature was kept below 20 °C. After stirring with ice-cooling for 30 minutes 3.1 mL of aqueous H_2O_2 (30 wt.-%) were added and the reaction mixture was stirred for an hour. It was then heated to 50 °C and stirred over night at this temperature. The reaction mixture was then diluted with water and extracted with ethyl acetate (3 x 100 mL). The combined organic phases were washed with aqueous Na_2SO_3 (2 x 50 mL) and dried over $MgSO_4$. After filtration and removal of the solvent, the crude product was purified by column chromatography over silica using CH_2Cl_2/EtOAc (9:1) as eluent. Recrystallization from heptane yielded the desired product as a white solid (1.8 g, 25 %).



^{1}H-NMR (CDCl$_3$, 25 °C, 600 MHz): δ 3.66 (s, 3H, H-1), 3.64 (t, $^3J_{H\text{-}H}$ = 6.8 Hz, 2H, H-8), 2.30 (t, $^3J_{H\text{-}H}$ = 7.6 Hz, 2H, H-3), 1.64-1.59 (m, 4H, H-4), 1.59-1.53 (m, 4H, H-7), 1.38-1.22 (m, 30H, H-5 and H-6).

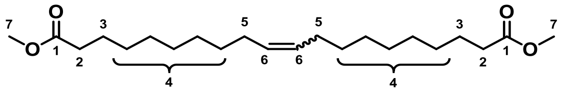
$^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C, 151 MHz): δ 174.49 (C-2), 63.26 (C-8), 51.58 (C-1), 34.28 (C-3), 32.99 (C-7), 29.94-29.28 (C-5), 25.90 (C-6), 25.13 (C-4).

Elemental analysis calculated for $C_{27}H_{54}O_3$: 76.00 % C, 12.76 % H; found: 75.61 % C, 12.69 % H.

Synthesis of Eicos-10-enedioic acid[13]

Degassed 10-undecenoic acid (55.3 g, 0.3 mol) was mixed with [$(PCy_3)_2Cl_2Ru{=}CHPh$] (Grubbs 1st generation catalyst) (0.6 mmol, 0.2 mol-%) under an argon flow. The reaction mixture was exposed to vacuum and stirred with a magnetic stir bar at room temperature for four hours. An off-white solid began to precipitate and the reaction was quenched with ethyl vinyl ether (10 mL). The off-white solid was filtrated at 5 °C and washed with pentane.

For esterification the resulting diacid was suspended in 200 mL of methanol. After addition of 8 drops of sulfuric acid, the resulting mixture was heated at 70 °C for 30 minutes. Dimethyl-1,20-eicos-10-enedioate (15.5 g, 29 %) was obtained in polymerization grade purity (≥ 99 %) by repeated recrystallization from methanol.



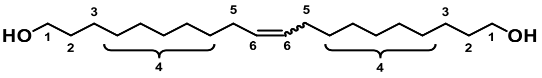
^{1}H-NMR ($CDCl_3$, 25 °C, 400 MHz): δ 5.39-5.35 (m, 2H, H-6), 3.66 (s, 6H, H-7), 2.30 (t, $^3J_{H\text{-}H}$ = 7.3 Hz, 4H, H-2), 2.00-1.92 (m, 4H, H-5), 1.66-1.57 (m, 4H, H-3), 1.36-1.22 (m, 20H, H-4).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C, 101 MHz): δ 174.47 (C-1), 130.48 (C-6), 51.58 (C-7), 34.27 (C-2), 32.73 (C-5), 29.86-29.14 (C-4), 25.11 (C-3).

Elemental analysis calculated for $C_{22}H_{40}O_4$: 71.70 % C, 10.94 % H; found: 71.86 % C, 10.78 % H.

Synthesis of Eicos-10-ene-1,20-diol

Dimethyl-1,20-eicos-10-enedioate (8.1 g, 22.0 mmol) was dissolved in 100 mL of THF and cooled with an ice bath. $LiAlH_4$ (2.0 g; 52.8 mmol) was added slowly within 30 minutes. The reaction mixture was stirred at room temperature for five hours and subsequently heated to reflux for half an hour. After stirring over night at room temperature the reaction was quenched by slow addition of 2.5 mL of water, 2.5 mL of 15 % aqueous NaOH and 5.0 mL of water. The reaction mixture was then filtrated at 50 °C over celite. After removing the solvent *in vacuo*, eicos-10-ene-1,20-diol was recrystallized from heptane to yield 5.6 g (81 %) of the pure product.



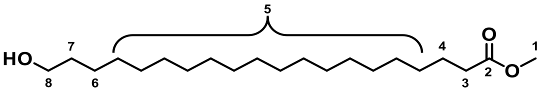
^{1}H-NMR ($CDCl_3$, 25 °C, 400 MHz): δ 5.40-5.30 (m, 2H, H-6), 3.63 (t, $^3J_{H\text{-}H}$ = 6.6 Hz, 4H, H-1), 2.00-1.92 (m, 4H, H-5), 1.60-1.51 (m, 4H, H-2), 1.40-1.22 (m, 24H, H-3 and H-4).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C, 101 MHz): δ 130.51 (C-6), 63.23 (C-1), 32.96 (C-2), 32.72 (C-5), 29.91-29.06 (C-4), 25.90 (C-3).

Elemental analysis calculated for $C_{20}H_{40}O_4$: 76.86 % C, 12.90 % H; found: 77.04 % C, 12.67 % H.

Synthesis of Methyl 20-hydroxyeicosanoate

Eicos-10-ene-1,20-diol (5.3 g, 17.0 mmol) was suspended in 100 mL of acetone and [Pd(dtbpx)(OTf)$_2$] (135.8 mg, 0.17 mmol) was added. The reaction mixture was stirred for two hours at room temperature and the solvent was removed *in vacuo*. The crude product was suspended in 60 mL of methanol and 2.5 mL of concentrated HCl (≥ 37 %) were added drop-wise at 4 °C. During the addition, the internal temperature was kept below 20 °C. After stirring with ice-cooling for 30 minutes 3.1 mL of aqueous H_2O_2 (30 wt.-%) were added and the reaction mixture was stirred for one hour. The mixture was heated to 50 °C and stirred over night at this temperature. The reaction mixture was then diluted with water and extracted with ethyl acetate (3 x 100 mL). The combined organic phases were washed with aqueous Na_2SO_3 (2 x 50 mL) and dried over $MgSO_4$. After filtration and removal of the solvent, the crude product was purified by column chromatography over silica using CH_2Cl_2/EtOAc (9:1) as eluent. After recrystallization from heptane the desired product was obtained as a white solid (2.3 g, 39 %).



^{1}H-NMR (CDCl$_3$, 25 °C, 600 MHz): δ 3.66 (s, 3H, H-1), 3.64 (t, $^3J_{H-H}$ = 6.7 Hz, 2H, H-8), 2.34 (t, $^3J_{H-H}$ = 7.4 Hz, 2H, H-3), 1.67-1.61 (m, 4H, H-4), 1.61-1.56 (m, 4H, H-7), 1.37-1.22 (m, 30H, H-5 and H-6).

^{13}C{^{1}H} NMR (CDCl$_3$, 25 °C, 151 MHz): δ 174.52 (C-2), 63.26 (C-8), 51.60 (C-1), 34.28 (C-3), 32.98 (C-7), 29.91-29.28 (C-5), 25.89 (C-6), 25.12 (C-4).

Elemental analysis calculated for $C_{21}H_{42}O_3$: 73.63 % C, 12.36 % H; found: 73.54 % C, 12.58 % H.

APCI-MS: m/z = 384.3 (M^+ + H + MeCN)

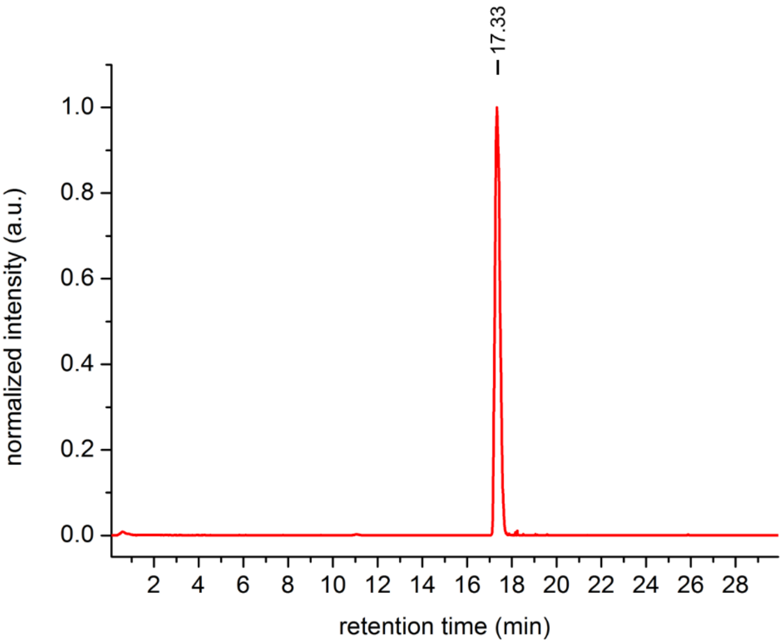


Figure 4.6: LC-MS chromatogramm of methyl 20-hydroxyeicosanoate.

4.4.3 Polymer synthesis

Polyesters were prepared in a 100 mL two-necked Schlenk tube equipped with an overhead stirrer. Efficient mixing of the highly viscous polymer melt was achieved by a helical agitator. Under a argon atmosphere the monomers (3.2 mmol of methyl 18-hydroxyoctadecanoate or methyl 20-hydroxyeicosanoate, respectively) were filled into the reaction vessel and molten by heating to 130 °C. A 1.2 mL solution of a 0.028 M titanium(IV) butoxide in toluene was injected, and the temperature was raised to 200 °C over the course of 8 h. Finally, the polymer melt was stirred overnight at this temperature under reduced pressure (0.01 mbar). Polyesters were analyzed by DSC, ^{1}H NMR and GPC measurements.

Poly[ω-hydroxyl octadecanoic acid] (10 K min^{-1}): T_m = 101 °C, T_c = 76 °C, and ΔH_m = 143 J g^{-1} (cf. **Figure 4.7**).

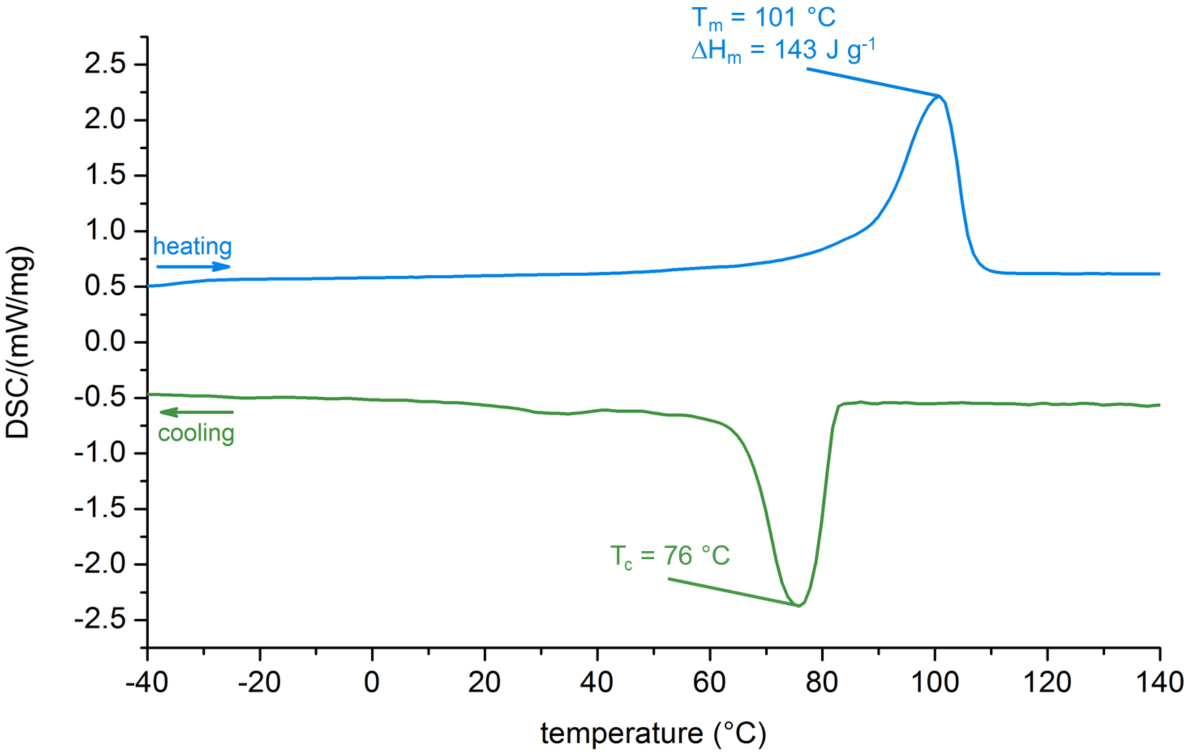


Figure 4.7: DSC trace of poly[ω-hydroxyl octadecanoic acid].

GPC reveals molecular weights M_n of typically 1.5×10^4 g mol^{-1} ($M_w/M_n = 4.2$) (cf. **Figure 4.8**); this data agrees with M_n of 1.6×10^4 g mol^{-1} determined from ^{1}H NMR spectroscopic analysis of the end groups.

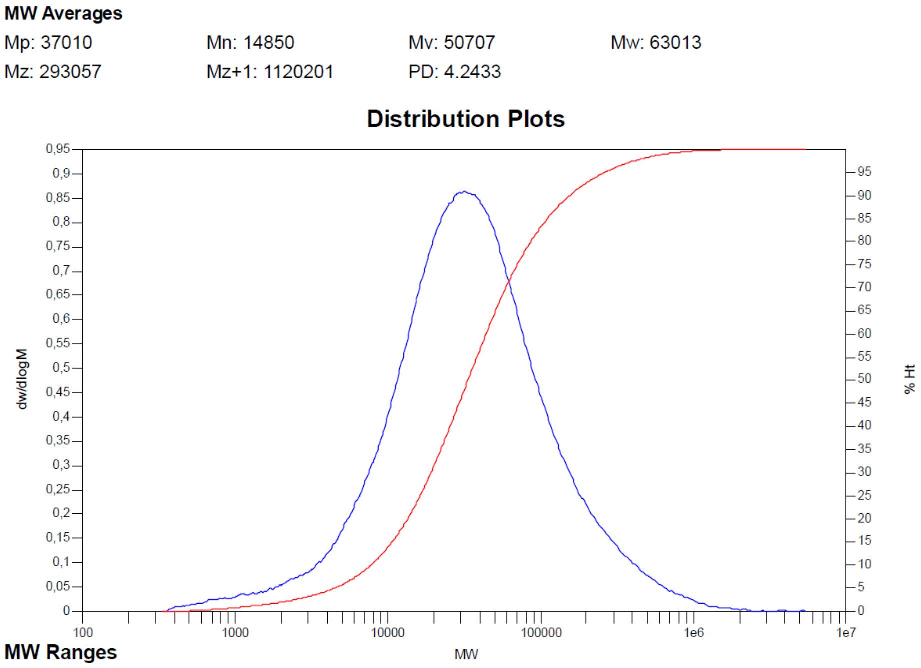


Figure 4.8: GPC trace of poly[ω-hydroxyl octadecanoic acid] (in 1,2,4-trichlorobenzene at 160 °C)

Poly[ω-hydroxyl eicosanoic acid] (10 K min^{-1}): T_m = 103 °C, T_c = 84 °C, and ΔH_m = 166 J g^{-1} (cf. **Figure 4.9**).

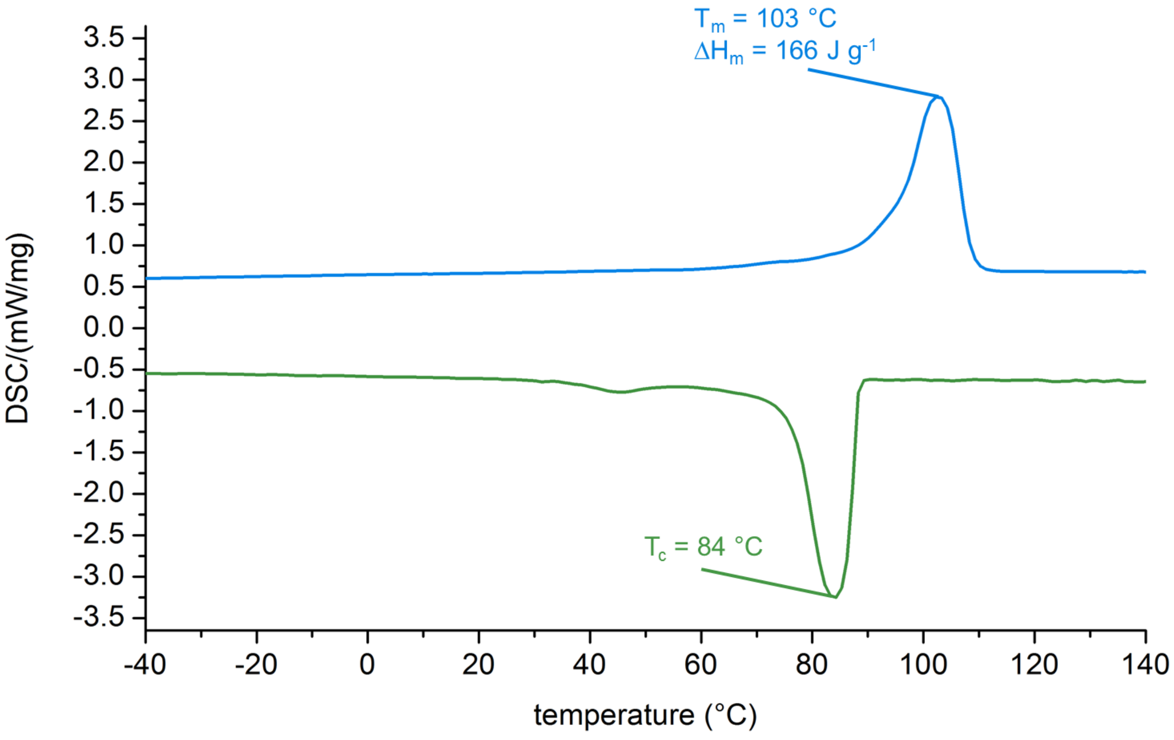
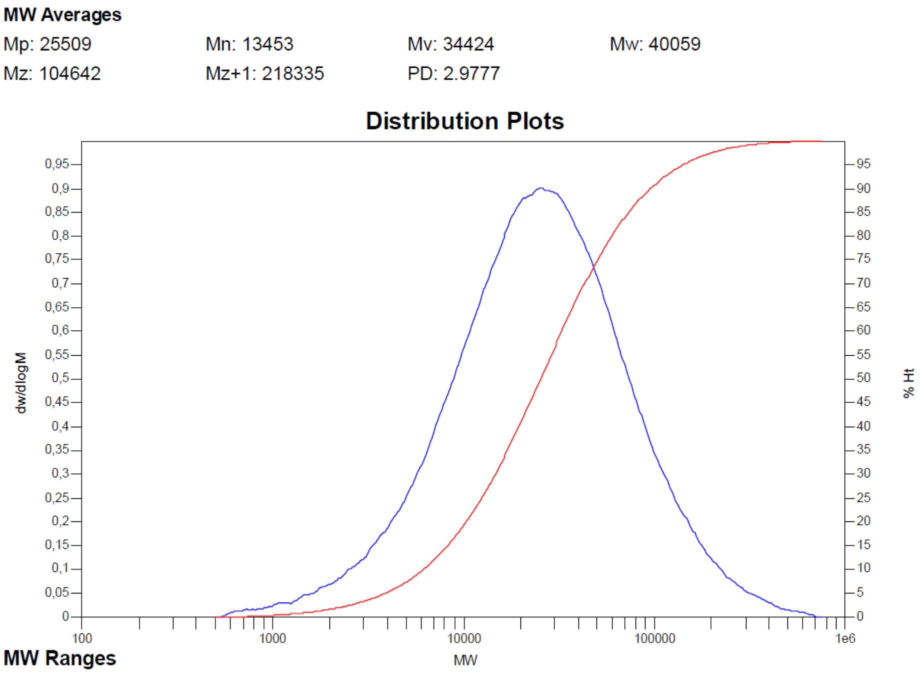


Figure 4.9: DSC trace of Poly[ω-hydroxyl eicosanoic acid].

GPC reveals molecular weights M_n of typically 1.3×10^4 g mol^{-1} ($M_w/M_n = 2.9$) (cf. **Figure 4.10**); this data agrees with M_n of 1.3×10^4 g mol^{-1} determined from ^{1}H NMR spectroscopic analysis of the end groups.



```
MW Averages
Mp: 25509          Mn: 13453          Mv: 34424          Mw: 40059
Mz: 104642         Mz+1: 218335       PD: 2.9777
```

Figure 4.10: GPC trace of poly[ω-hydroxyl eicosanoic acid] (in 1,2,4-trichlorobenzene at 160 °C)

4.5 References

1. Unsymmetrical α,ω-Difunctionalized Long-Chain Compounds via Full Molecular Incorporation of Fatty Acids. Witt, T.; Stempfle, F.; Roesle, P.; Häußler, M.; Mecking, S. *ACS Catalysis* **2015**, *5*, 4519-4529.
2. On Inventing Reactions for Atom Economy. Trost, B. M. *Acc. Chem. Res.* **2002**, *35*, 695-705.
3. Transposition of Allylic Alcohols into Carbonyl Compounds Mediated by Transition Metal Complexes. Uma, R.; Crévisy, C.; Grée, R. *Chem. Rev.* **2002**, *103*, 27-52.
4. Transition Metal Complexes as Catalysts of Double-Bond Migration in O-allyl Systems. Kuźnik, N.; Krompiec, S. *Coord. Chem. Rev.* **2007**, *251*, 222-233.
5. Dodecacarbonyl Triiron, an Efficient Catalyst for Photochemical Isomerization of Unsaturated Alcohols, Ethers and Ester to Their Corresponding Carbonyl Compounds, Enol Ethers and Esters. Iranpoor, N.; Mottaghinejad, E. *J. Organomet. Chem.* **1992**, *423*, 399-404.
6. Extensive Isomerization of Alkenes Using a Bifunctional Catalyst: An Alkene Zipper. Grotjahn, D. B.; Larsen, C. R.; Gustafson, J. L.; Nair, R.; Sharma, A. *J. Am. Chem. Soc.* **2007**, *129*, 9592-9593.
7. Self Metathesis of Fatty Alcohols and Amines to Provide Monomers for Polyester and Polyamide Products. Riepl, H. M.; Pettrak, J.; Faulstich, M.; Herrmann, W. A. *Macromol. Symp.* **2010**, *293*, 39-42.
8. a) Grubbs, R. H. *Handbook of Metathesis, Vol. 1-3*; Wiley-VCH: Weinheim, **2003**. b) Degradation of the Second-Generation Grubbs Metathesis Catalyst with Primary Alcohols and Oxygen - Isomerization and Hydrogenation Activities of Monocarbonyl Complexes. Dinger, M. B.; Mol, J. C. *Eur. J. Inorg. Chem.* **2003**, *15*, 2827-2833. c) Catalysis at the Interface of Ruthenium Carbene and Ruthenium Hydride Chemistry: Organometallic Aspects and Applications to Organic Synthesis. Schmidt, B. *Eur. J. Org. Chem.* **2004**, *9*, 1865-1880.
9. Ruthenium Carbene-Based Olefin Metathesis Initiators: Catalyst Decomposition and Longevity. Ulman, M.; Grubbs, R. H. *J. Org. Chem.* **1999**, *64*, 7202-7207.
10. Colquhoun, H. M.; Holton, J.; Thompson, D. J.; Twigg, M. V. in *New Pathways for Organic Synthesis*, Eds. Colquhoun, H. M.; Holton, J.; Thompson, D. J.; Twigg, M. V. Plenum Press: New York, **1984**; pp 173-193.
11. Chemical Methods for Treating a Metathesis Feedstock. Lemke, D. W.; Uptain, K. D.; Amore, F.; Abraham, T. (Elevance Renewable Sciences), WO 2009/020667 A1, **2009**.

12. a) Phenylphosphoric Acid as a New Additive to Inhibit Olefin Isomerisation in Ruthenium-Catalysed Metathesis Reactions. Gimeno, N.; Formentín, P.; Steinke, J. H. G.; Vilar, R. *Eur. J. Org. Chem.* **2007**, *2007*, 918-924. b) Prevention of Undesirable Isomerization during Olefin Metathesis. Hong, S. H.; Sanders, D. P.; Lee, C. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **2005**, *127*, 17160-17161.
13. Aliphatic Long-Chain C_{20} Polyesters from Olefin Metathesis. Trzaskowski, J.; Quinzler, D.; Bährle, C.; Mecking, S. *Macromol. Rapid Commun.* **2011**, *32*, 1352-1356.
14. a) Comparison of the Kinetics of Acyclic Diene Metathesis Promoted by Grubbs Ruthenium Olefin Metathesis Catalysts. Lehman, S. E.; Wagener, K. B. *Macromolecules* **2001**, *35*, 48-53. b) Olefin Isomerization Promoted by Olefin Metathesis Catalysts. Lehman Jr, S. E.; Schwendeman, J. E.; O'Donnell, P. M.; Wagener, K. B. *Inorg. Chim. Acta* **2003**, *345*, 190-198. c) Improving the Selectivity for the Synthesis of Two Renewable Platform Chemicals via Olefin Metathesis. Djigoué, G. B.; Meier, M. A. R. *Appl. Catal. A* **2009**, *368*, 158-162.
15. Terpene-Based Renewable Monomers and Polymers via Thiol-Ene Additions. Firdaus, M.; Montero de Espinosa, L.; Meier, M. A. R. *Macromolecules* **2011**, *44*, 7253-7262.
16. a) Mechanistic Features of Isomerizing Alkoxycarbonylation of Methyl Oleate. Roesle, P.; Dürr, C. J.; Möller, H. M.; Cavallo, L.; Caporaso, L.; Mecking, S., *J. Am. Chem. Soc.* **2012**, *134*, 17696-17703. b) A Comprehensive Mechanistic Picture of the Isomerizing Alkoxy-carbonylation of Plant Oils. Roesle, P.; Caporaso, L.; Schnitte, M.; Goldbach, V.; Cavallo, L.; Mecking, S. *J. Am. Chem. Soc.* **2014**, *136*, 16871-16881.
17. Direct Oxidation of Acetals and Aldehydes to Esters. Takeda, T.; Watanabe, H.; Kitahara, T. *Synlett* **1997**, *10*, 1149-1150.
18. a) Thermoplastic Polyesters and Co-Polyesters derived from Vegetable Oil: Synthesis and Optimization of Melt Polycondensation for Medium and Long Chain Poly(ω-hydroxyfatty acid)s and their Ester Derivatives. Jose, J.; Pourfallah, G.; Merkley, D.; Li, S.; Bouzidi, L.; Leao, A. L.; Narine, S. S. *Polymer Chemistry* **2014**, *5*, 3203-3213. b) Influence of Monomeric and Polymeric Structure on the Physical Properties of Thermoplastic Polyesters derived from Hydroxy Fatty Acids. Jose, J.; Pourfallah, G.; Leao, A. L.; Narine, S. S. *Polym. Int.* **2014**, *63*, 1902-1911.
19. Large-Ring Lactones from Plant Oils. Witt, T.; Mecking, S. *Green Chemistry* **2013**, *15*, 2361-2364.
20. Long-Chain Linear C_{19} and C_{23} Monomers and Polycondensates from Unsaturated Fatty Acid Esters. Stempfle, F.; Quinzler, D.; Heckler, I.; Mecking, S. *Macromolecules* **2011**, *44*, 4159-4166.

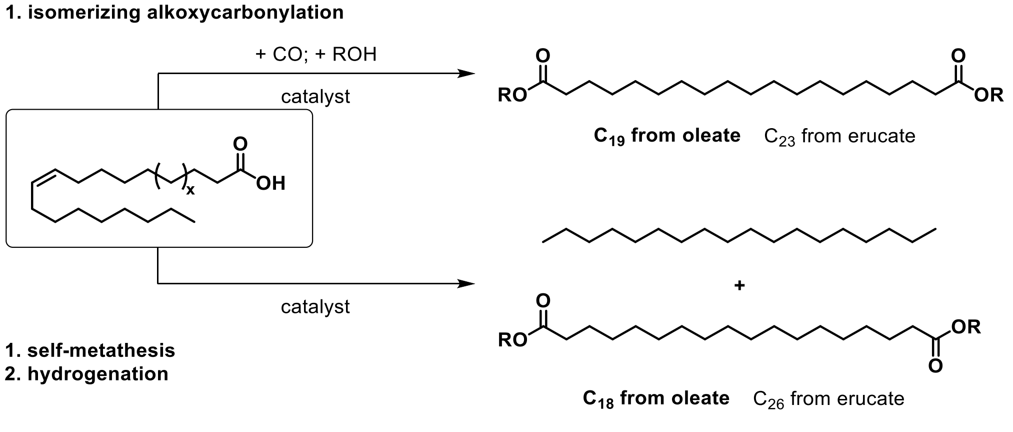
5 Material properties of long-chain aliphatic polyesters

5.1 Introduction

Dicarboxylic acids derived from plant oils are attractive intermediates for the synthesis of polymer materials.[1] The incorporation of long methylene sequences enables polymer crystallization similar to polyethylene and renders polyesters more hydrophobic. Long-chain aliphatic polyesters that incorporate the full length of the plant oils methylene sequences possess high melting points ($T_m > 100$ °C) and crystallization temperatures, suitable for thermoplastic processing. This differs from their shorter chain analogs. Here, the incorporation of aromatic comonomers such as terephthalic acid is required in order to improve the crystallization temperature, heat distortion temperature and mechanical properties of aliphatic polyesters.[2]

More recently, entirely chemical catalytic conversions of plant oils have complemented the existing approach of biotechnological ω-oxidation as a route to long-chain aliphatic monomers.[3,4] As outlined in chapter 1 and 3, self-metathesis[5-9] generates (after subsequent double bond hydrogenation) a long-chain α,ω-diacid ester along with a stoichiometric amount of linear hydrocarbon as the main products (**Scheme 5.1**). In this context, the implementation of the commercial-scale refining of palm oil to chemicals by metathesis with 1-butene is notable.[10,11] Due to the specifics of the process and of olefin metathesis in general, a significant amount of self-metathesis will occur as a side reaction to yield 1,18-octadecene dioate.[12]

A different route has recently been found with isomerizing alkoxycarbonylation (**Scheme 5.1**).[13-15] Other than metathesis, the long-chain methylene sequence of the fatty acid feedstock is fully incorporated into the α,ω-diacid ester product. This is a result of the highly kinetically controlled outcome of the isomerizing alkoxycarbonylation reaction *vs.* the equilibrium product distribution from metathesis.[16]



Scheme 5.1: Main products of the isomerizing alkoxycarbonylation and self-metathesis, respectively, of unsaturated fatty acid esters.

Polycondensation reactions are well established and used widely in industry for the synthesis of, amongst others, polyesters. Nonetheless, obtaining sufficient molecular weight for achieving entanglement and mechanical strength is not trivial for a given set of monomers. Typically, polyester molecular weights are in the range of 10^4 to 5×10^4 g mol^{-1} in order to prevent embrittlement and premature mechanical failure on straining. Molecular weights of polyesters or polyamides prepared by step-growth polycondensation are highly sensitive to the presence of impurities and require extremely high purity and accurate stoichiometry of the difunctional monomers. Obtaining a material with useful mechanical properties from a new type of monomer is always precarious, and there is no generic protocol. For example, most A_2+B_2 syntheses of polyester materials employ a diol which is volatile to a relevant extent under polycondensation conditions such that it can be used in excess in the initial reaction mixture. This does not apply to the polyesters studied here. Due to these and other general limitations only little is known about the material properties of such entirely long-chain aliphatic polyesters based on symmetric α,ω-functionalized monomers.

This chapter now provides the mechanical properties of entirely aliphatic semicrystalline polyesters based on linear long-chain dicarboxylic acids and diols, which were previously reported by our group.[14,15]

5.2 Results and discussion

5.2.1 Monomer and polymer synthesis

Isomerizing alkoxycarbonylation was utilized to gain access to long-chain linear aliphatic diesters and diols. High oleic sunflower oil methyl ester (Dakolub MB9001) or technical grade methyl erucate, respectively, were used as a starting material. A well-defined catalyst precursor, [1,2-bis-{(di-*tert*-butylphosphino)methyl}benzene palladium ditriflate][15] was employed. This is signifycantly more efficient by comparison to catalysts obtained by mixing a palladium source and the diphosphine *in situ*, which requires a five-fold excess of the diphosphine.[17,18] As a prerequisite for the studies of polyesters reported here, the monomer synthesis was investigated on an enhanced scale in a 1L pressure reactor (**Table 5.1**).

Table 5.1: Monomer synthesis by isomerizing alkoxycarbonylation.[a]

entry	substrate	conversion[b] [%]	selectivity[b] [%]	isolated yield of pure product
1	methyl oleate	89 %	89 %	115 g (76 %)
2	methyl erucate	72 %	84 %	96 g (54 %)

[a] conditions: 430 mmol substrate, 0.86 mmol [(dbpx)Pd(OTf)$_2$], 550 mL MeOH 20 bar CO, 90 °C, 120 h. [b] Determined by GC analysis of the crude reaction mixture.

No adverse effects on productivity, selectivity or product purity *vs.* smaller scale syntheses[15] was observed. Upon crystallization from methanol, used as the reaction medium, the linear C_{19} and C_{23} diester were obtained on a 100 g scale in > 99 % purity. The residual filtrate predominantly consists of (isomerized) starting material and in principle can be reused again.

Long-chain α,ω-diol monomers were generated by reduction of the aforementioned diesters, stoichiometrically with $LiAlH_4$ or by catalytic hydrogenation with Saudan's[19] ruthenium catalyst. In addition, preliminary experiments showed that catalytic reduction is also possible using a ruthenium hydride complex based on the pincer ligand PNN (2-(di-*tert*-butylphosphinomethyl)-6-(diethylaminomethyl)pyridine) developed by Milstein and coworkers.[20]

Previous work by our laboratory demonstrated that polycondensation of stoichiometric amounts of these difunctional A_2+B_2 monomers catalyzed by titanium alkoxides afforded the corresponding long-chain aliphatic polyesters, namely poly[1,19-nonadecadiyl-1,19-nonadecanedioate] (**PE-19.19**) and poly[1,23-tricosadiyl-1,23-tricosanedioate] (**PE-23.23**).[14] GPC measurements in 1,2,4-trichlorobenzene at 160 °C *vs.* linear polyethylene standards of these novel polycondensates revealed molecular weights M_w of typically 2 x 10^4 g mol^{-1} (M_w/M_n = 2). However, in order to elucidate the polyesters' materials properties higher molecular weights are required and also polymer quantities have to be enhanced.

Optimization of the polycondensation reaction to linear long-chain aliphatic polyesters

Despite their large scale applications, polycondensations to sufficient molecular weights for achieving entanglement and mechanical strength are challenging and no generic protocols exist that can be transferred to a new combination of monomers of interest. For this reason polymerization conditions have to be adopted to the characteristics of the monomers applied.

Reaction conditions for the polycondensation to linear long-chain aliphatic polyesters were optimized starting from commercially available octadecanedioic acid marketed by Emery Oleochemicals under the trade name Emerox118®.[21] After purification by transesterification and subsequent recrystallization from methanol, dimethyl-1,18-octadecanedioate was reduced to the corresponding α,ω-diol. With sufficient amount of these two α,ω-difunctional monomers in our hand, polycondensations were optimized using 16 mmol of either monomer, affording between 5 and 10 g of polyester.

However, first polycondensation experiments on this scale clearly pointed out that no efficient mixing of the highly viscous polymer melt is provided using our standard polymerization equipment.

Figure 5.1: Optimized polymerization equipment with a helical stirrer.

Thus in order to achieve effective mixing throughout the whole polycondensation process, a new helical agitator was designed (**Figure 5.1**). Furthermore the diameter of the polycondensation schlenk tubes was increased to facilitate circulation of the polymer melt (**Figure 5.2**)

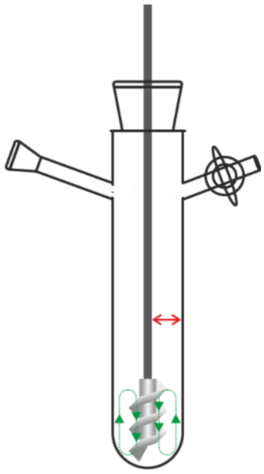


Figure 5.2: Schematic representation of the optimized polymerization equipment with a helical agitator and corresponding diameter of the Schlenk tube

Polycondensation employing this revised equipment, applying 0.5 mol-% of titanium butoxide as catalyst, yields **PE-18.18** with a number average molecular weight of M_n 2.9 x 10^4 g mol^{-1} as determined by high temperature size exclusion chromatography (cf. **Table 5.2**, entry 1).

Table 5.2: Polycondensation to **PE-18.18** applying different amounts of catalyst.

entry	$Ti(OBu)_4$	$M_{n,GPC}$^{b} [g mol^{-1}]	$M_{w,GPC}$^{b} [g mol^{-1}]	M_w/M_n^{b}
1	0.5 mol-%	2.9 × 10^4	3.0 × 10^4	2.6
2	0.5 mol-% in 0.6 mL Toluene	3.5 × 10^4	9.4 × 10^4	2.7
3^c	0.5 mol-% in 0.6 mL Toluene	1.4 × 10^4	6.7 × 10^4	4.7
4	0.05 mol-% in 0.6 mL Toluene	3.7 × 10^4	8.4 × 10^4	2.3
5	0.005 mol-% in 0.6 mL Toluene	1.7 × 10^4	4.7 × 10^4	2.8

a) conditions: 16.0 mmol of dimethyl-1,18-octadecanedioate and octadecane-1,18-diol, temperature was gradually increased to 200 °C over the course of 8 h; finally, the polymer melt was stirred for about 16 h at this temperature under reduced pressure (0.01 mbar) b) Determined by GPC at 160 °C in trichlorobenzene *vs.* polyethylene standards. c) Final polycondensation temperature of 230 °C.

By dissolving the catalyst in dry and degassed toluene molecular weights could be further increased as the refluxing toluene solution is washing down residual monomer from the glass tube at the beginning of the polycondensation process (cf. **Table 5.2**, entry 2). Even higher molecular weights of M_n 3.7 × 10^4 g mol^{-1} were obtained by reducing the catalyst loading to 0.05 mol-% (cf. **Table 5.2**, entry 4). However, decreasing the amount of catalyst to 0.005 mol-% resulted in a decrease of the number average molecular weight (cf. **Table 5.2**, entry 5). Besides catalyst loading, also the polycondensation temperature was varied. Effective mixing of the polymer melt was enhanced by increasing the final temperature to 230 °C and thus decreasing the viscosity of the polymer melt. Nevertheless molecular weights did not increase due to thermal degradation of the polymer under these harsh conditions, indicated by the brownish color of the resulting polymer and the relative broad polydispersity observed for this sample (cf. **Table 5.2**, entry 3).

After this optimization, polymerizations of the C_{19} as well as the C_{23} components were typically performed on a scale of 20 mmol of either monomer, affording between 10 and 15 g of polyester (**Table 5.3**).[b] Optimized reaction conditions essentially comprised 0.05 mol-% of $Ti(OBu)_4$ and stirring for 16 hours at 200 °C and 0.01 mbar with a helical agitator (cf. Experimental section). Polymerization under these conditions and on this scale yielded polyesters with a number average molecular weight of M_n 3.0×10^4 g mol^{-1} as determined by both ^{1}H-NMR quantification of end-groups and high temperature GPC relative to polyethylene standards. In view of the largely polyethylene-like character of the polymer chains, GPC *vs.* polyethylene standards appears most appropriate by comparison to other common standards.

Table 5.3: Molecular weights and thermal properties of long-chain aliphatic polyesters.

entry	T_m[a] [°C]	T_c[a] [°C]	$M_{n,NMR}$[b] [g mol^{-1}]	$M_{n,GPC}$[c] [g mol^{-1}]	M_w/M_n[c]
PE-19.19	102	83	2.9×10^4	3.0×10^4	2.6
PE-23.23	107	86	3.9×10^4	3.9×10^4	2.4

a) Determined by DSC with a heating/cooling rate of 10 K min^{-1}.
b) Determined by end-group analysis from ^{1}H-NMR spectroscopy.
c) Determined by GPC at 160 °C in trichlorobenzene *vs.* polyethylene standards.

Regarding the investigation of the material properties of these new materials, this increase in molecular weight is essential, as for example polymer samples of lower molecular weights do not exhibit a steady state behavior during rheological measurement. Time sweep experiments of **PE-23.23** with a number average molecular weight of M_n 1.8×10^4 g mol^{-1} as determined by high temperature GPC relative to polyethylene standards, at a constant temperature T = 130 °C and constant frequency $\omega = 10$ rad/s, show a significant increase in storage modulus (G`) as well as loss modulus (G``) over time (**Figure 5.3**). This buildup in modulus can be attributed to chemical or physical changes in the melt such as further reactions of end-groups. However, a resulting change in molecular weight could not be evidenced neither by GPC measurements nor by end-group analysis by ^{1}H-NMR spectroscopy, of the polymer samples before and after the time sweep.

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[b] For polyester-19.19 prepared on a larger scale of 50 mmol, essentially identical molecular weights and tensile properties were observed.

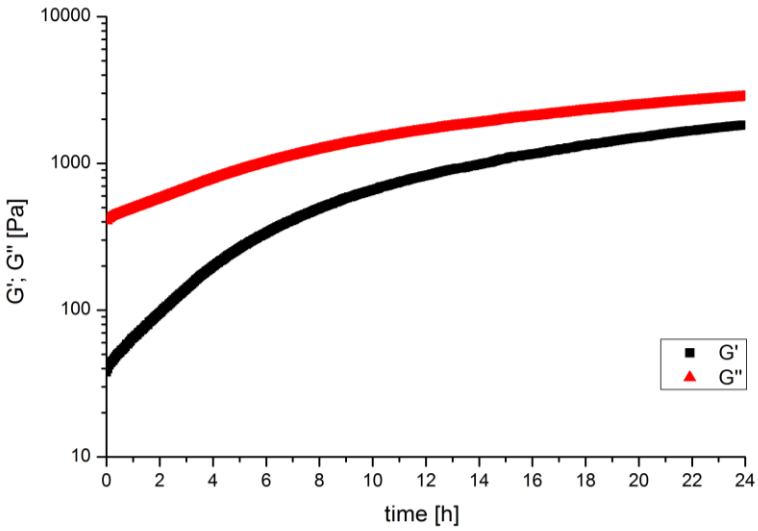

Figure 5.3: Time sweep measurement of **PE-23.23** with a number average molecular weight of $M_{n,GPC}$ 1.8×10^4 g mol^{-1} (T = 130 °C, $\omega = 10$ rad/s, $\gamma = 6$ %, gap = 0.5 mm).

By contrast, polyesters of higher molecular weight generated by the above protocol were confirmed to be sufficiently stable during a typical experiment. In view of melt processing, required amongst others for the preparation of samples for tensile testing (*vide infra*), they display a simple rheological behavior (**Figure 5.4** and Experimental section). The storage modulus (G`) and loss modulus (G``) can be superimposed only by horizontal shifts along the frequency axis.[22] This shows that no undesired chemical or physical changes occur in the melt, such as changes of molecular weight by degradation, further reactions of end-groups, or crosslinking.

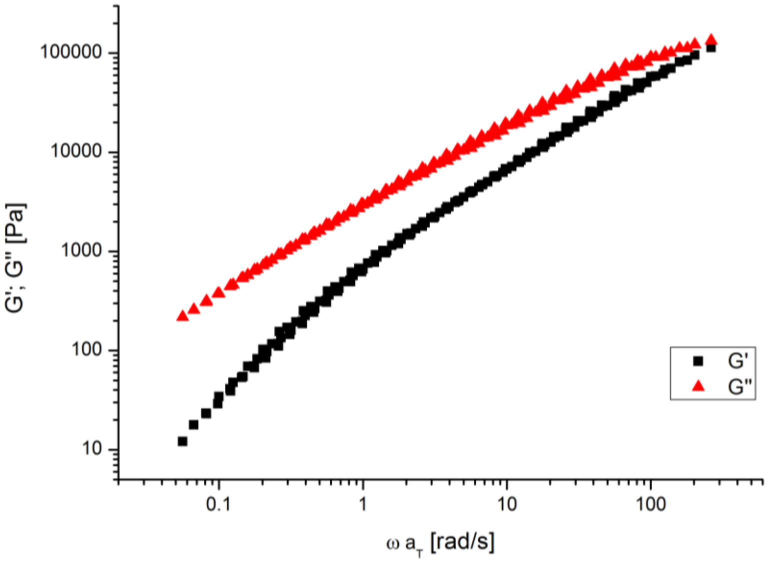

Figure 5.4: Master curves of G` and G`` for **PE-19.19** (from measurements at 110, 120, 130, 140, 150, 160, 180 and 190 °C). Shifting temperature is 150 °C.

5.2.2 Tensile properties

For tensile testing of **PE-19.19** and **PE-23.23**, dog-bone shaped test specimen were obtained by injection molding using a mini-compounder (cf. Experimental section).

Figure 5.5: Dog-bone-shaped sample bar for tensile testing.

In the first tests applying polymer samples with a number average molecular weight between 1.0 and 2.0×10^4 g mol^{-1}, as determined by high temperature GPC, brittle fracture was observed, indicating that the molecular weight of the material was likely insufficient to enable effective chain entanglement. **PE-23.23** for example exhibited a Young's modulus of 1500 MPa with an elongation of break of just 1.1 %.

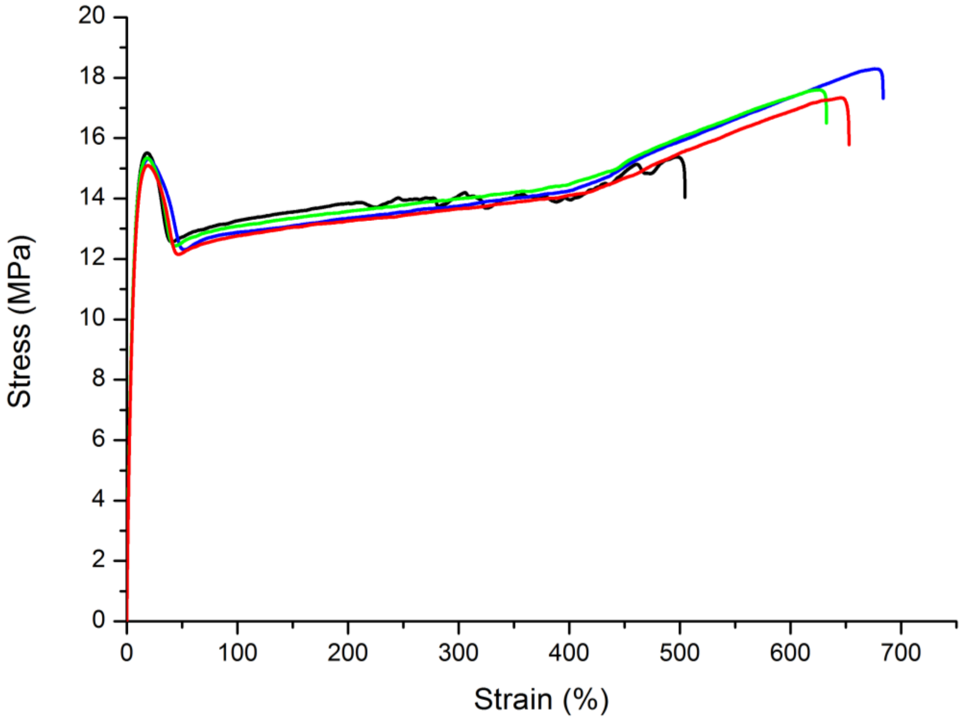

Figure 5.6: Stress-strain curves of **PE-19.19**.

However, **PE-19.19** and **PE-23.23** generated by the above protocol clearly show typical properties of a polymeric material rather than a brittle wax-like behavior. Following a linear and nonlinear viscoelasticity regime (I), a neck region with strain softening (II) and plastic flow (III), strain hardening (IV) is also observed as concluded from the characteristic changes of slope in the stress-strain curves (**Figure 5.6** and Experimental section).[23]

Both polyesters show Young's moduli around 400 MPa and an elongation at break of more than 600 % (**Table 5.4**).

Table 5.4: Tensile properties (Young's modulus, stress at yielding, strain at yielding, stress at break and elongation at break) of polyesters.[a]

entry	Young's Modulus [MPa]	Stress at yield [MPa]	Strain at yield [%]	Stress at break [MPa]	Elongation at break [%]
PE-19.19	408	15.3	18.3	15.9	619
PE-23.23	436	16.7	19.7	17.0	678

a) True stress at break calculated after cross-section area correction.

In detail, **PE-23.23** displays a slightly higher modulus *vs.* **PE-19.19**, as expected due to the higher crystallinity[14] arising from the longer methylene sequences. These tensile properties are similar to those of polyesters $[O(CH_2)_nC(O)]_x$ generated by ring-opening chain growth polymerization of naturally occurring pentadecalactone ($n = 15$)[24-26] or AB-polycondensation of 14-hydroxy-tetradecane carboxylic acid from enzymatic ω-hydroxylation of myristic acid ($n = 14$).[27] By comparison, high density polyethylene (HDPE) from linear insertion chain growth typically displays a Young's modulus of ca. 1 GPa.[28]

Also the shore D hardness increases with increasing chain length of the repeat units' hydrocarbon segments from 54 for **PE-19.19** to 56 for **PE-23.23**. This approaches the hardness of 60 to 70 given for HDPE.[29]

5.2.3 Dynamic mechanical analysis

As a result of the high degree of crystallinity χ of about 70 % for **PE-19.19** and 75 % of **PE-23.23** as determined by wide-angle X-ray scattering,[14] even upon rapid cooling or heating in DSC no glass transitions could be observed reliably due to the small portion of amorphous polymer subject to vitrification or softening, respectively. Dynamic mechanical analyses (DMA, at a frequency of 1 Hz) were more conclusive to this end. For **PE-19.19** from the loss modulus *vs.* temperature a T_g of -37 °C was observed (**Figure 5.7**). The longer-chain aliphatic polyester **PE-23.23** exhibits a slightly higher glass-transition temperature of -27 °C (cf. Experimental section).

This difference can be ascribed to the enhanced crystallinity due to the longer methylene sequences and the resulting stronger restriction in mobility.[30, c]

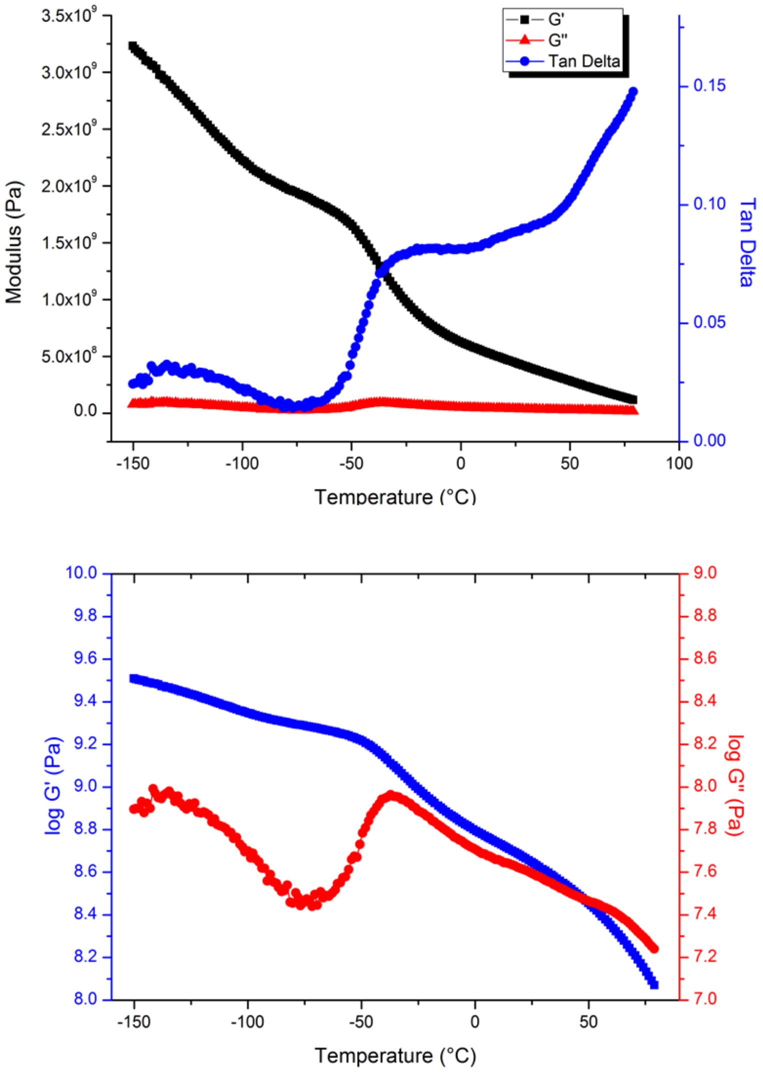

Figure 5.7: Dynamic mechanical analysis of **PE-19.19**.

Besides the relaxation due to the glass transition, both polymers show a second relaxation phenomenon at around -130 °C, which can be ascribed to the motion of the methylene sequences of the polyester main chain.[31,32]

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[c] For poly(ω-hydroxyl tetradecanoic acid) (**PE-14**) a T_g of −30 °C has been reported,[27] and for poly(ω-pentadecalactone) (**PE-15**) a T_g of −27 °C.[32]

5.2.4 Hydrolytic degradation

Preliminary hydrolytic degradation studies were performed on solid samples in concentrated and diluted acidic and basic aqueous media. Beyond first insights into the behavior of the material towards these media, the experiments to some extent also allow for an estimation of the behavior over longer terms but under milder conditions.

For the hydrolytic cleavage experiments, pellets of long-chain aliphatic polyester **PE-19.19** (prepared by injection molding using a mini-compounder, cf. Experimental section) were exposed to 20 wt.-% aq. NaOH, 1 M aq. HCl and concentrated aq. HCl at elevated temperatures (T = 40 °C). With time intervals of a week, the pellets were removed, washed with water and acetone and dried at room-temperature under vacuum for 24 h. After determination of the weight loss the media were renewed and the polymer samples were again exposed to the corresponding acidic or basic medium. After four weeks of exposure, weight losses for all the samples were still within the error of the method.[d] However, the appearance and surface structure changed significantly (**Figure 5.8**).

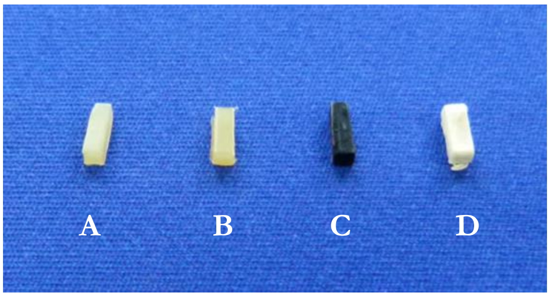

Figure 5.8: Pellets of polyester **PE-19.19** before (A) and after four weeks of hydrolytic degradation at 40 °C in 1 M aq. HCl (B), concentrated aq. HCl (C) and 20 wt.-% aq. NaOH (D).

The pellets in conc. aq. HCl (**Figure 5.8**, C) for example turned black, whereas the polymer samples exposed to 20 wt.-% aq. NaOH (**Figure 5.8**, D) had an increased surface roughness and showed whitening at the edges. After another three weeks in the corresponding media the latter ones even broke up into pieces (hampering an exact weight loss determination), whereas the pellets in acidic media still remained intact, without showing any significant weight loss (**Figure 5.9**).

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[d] A maximum error of 1 % can be assumed for pellet weight determination.

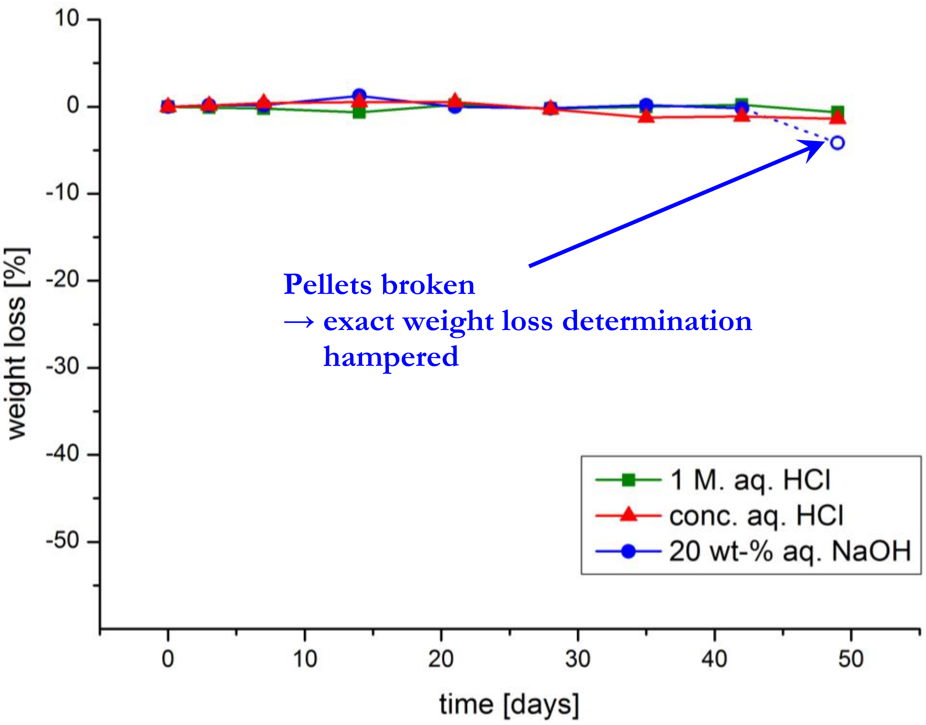


Figure 5.9: Hydrolytig degradation of **PE-19.19** pellets in 20 wt.-% aq. NaOH, 1 M aq. HCl and concentrated aq. HCl at 40 °C. Average weight loss as a function of degradation time.

For pellets of **PE-19.19** in PBS puffer (pH = 7.4) at 40 °C neither mass loss nor a change in appearance or surface roughness was observed over seven weeks. This is in accordance with hydrolytic degradation studies of poly(ω-pentadecalactone), which do not show degradation over a period of two years.[33] One reason for the hydrolytic stability of these long-chain aliphatic polyesters might be the high crystallinity and hydrophobicity of these new materials. This prevents the penetration of the medium into the materials to initiate degradation.

Although all these experiments provide first insights into the behavior of long-chain aliphatic polyesters towards hydrolytic degradation further experiments, in particular comparison with other aliphatic polyesters of shorter chain length, are required. Furthermore as change of mechanical properties due to degradation is often observed before detection of any polymer weight loss, also monitoring the material properties during hydrolytic degradation might be of interest.

5.3 Conclusion

Isomerizing alkoxycarbonylation was utilized to gain access to long-chain α,ω-diacid ester monomers. Starting from technical grade methyl ester of high oleic sunflower oil dimethyl-1,19-nonadecanedioate was obtained in polycondensation grade purity. Likewise, dimethyl-1,23-tricosanedioate was derived from methyl erucate. The successful 'scale-up' renders both intermediates available on a 100 g scale. The corresponding long-chain α,ω-diol components were generated by catalytic hydrogenation with Saudan's[19] ruthenium catalyst, but also catalytic reduction using a ruthenium hydride complex based on the pincer ligand PNN (2-(di-*tert*-butylphosphinomethyl)-6-(diethylaminomethyl)pyridine) developed by Milstein and coworkers was possible.[20]

Polycondensation of both the C_{19} and the C_{23} components applying optimized polymerizations conditions afforded between 10 and 15 g of long-chain aliphatic polyesters, namely poly[1,19-nonadecadiyl-1,19-nonadecanedioate] (**PE-19.19**) and poly[1,23-tricosadiyl-1,23-tricosanedioate] (**PE-23.23**). The produced polymers exhibit a number average molecular weight of M_n $3.0 \times 10^4\,\text{g mol}^{-1}$ as determined by both ^{1}H-NMR quantification of end-groups and high temperature GPC relative to polyethylene standards. Both materials possess an elongation at break of > 600 % and a Young's modulus of around 400 MPa. Furthermore first tests on the hydrolytic degradation revealed good stability of these new materials in concentrated and diluted acidic and basic aqueous media. Considering their reasonably high melt and crystallization temperatures, these findings all point out that useful and attractive materials properties can be achieved for aliphatic polyesters generated by polycondensation of long-chain aliphatic diacids with long-chain diols and offer prospects for novel bio-based films or moldings.

5.4 Experimental section

5.4.1 Materials and general considerations

Unless stated otherwise, all manipulations were carried out under an inert gas atmosphere using standard Schlenk or glovebox techniques. Methanol was distilled from magnesium turnings and iodine prior to use. Toluene was distilled from sodium and THF from sodium/benzophenone. All other solvents were used in technical grade as received. Carbon monoxide (3.7) and hydrogen (5.0) were supplied by Air Liquide. [Pd(dtbpx)(OTf)$_2$] was prepared according to a reported procedure.[15] High oleic sunflower oil methyl ester (92.5 % of methyl oleate) supplied by Dako AG and methyl erucate (>90 %) from TCI were degassed prior to use. Sodium methoxide (95 %), titanium(IV) butoxide (≥ 97%) and (±)-α-tocopherol (synthetic, ≥ 96%) were purchased from Sigma Aldrich. All deuterated solvents were supplied by Eurisotop.

NMR spectra were recorded on a Varian Inova 400. ^{1}H and ^{13}C chemical shifts were referenced to the solvent signals. High-temperature NMR measurements of polymers were performed in 1,1,2,2-tetrachloroethane-*d2* at 130 °C.

DSC analyses were performed on a Netzsch Phoenix 204 F1 instrument with a heating and cooling rate, respectively, of 10 K min^{-1}. Data reported are from second heating cycles.

High temperature GPC measurements were carried out in 1,2,4-trichlorobenzene at 160 °C at a flow rate of 1 mL min^{-1} on a Polymer Laboratories 220 instrument equipped with Olexis columns with differential refractive index, viscosity, and light-scattering (15° and 90°) detectors. Data reported were determined directly against polyethylene standards.

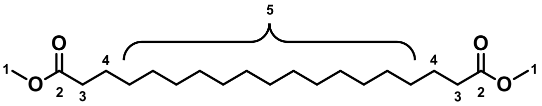
Gas chromatography was carried out on a PerkinElmer (PE) Clarus 500 instrument with an autosampler and FID detection on a PerkinElmer Elite-5 (5 % diphenyl - 95 % dimethylpolysiloxane) Series Capillary Columns (length: 30 m, inner diameter: 0.25 mm, film thickness: 0.25 mm), using helium as a carrier gas at a flow rate of 1.5 mL min^{-1}. The injector temperature was 300 °C. After injection the oven was kept isothermal at 90 °C for 1 min, heated at 30 K min^{-1} to 280 °C, and kept isothermal at 280 °C for 8 min.

5.4.2 Monomer synthesis

Alkoxycarbonylations of unsaturated long-chain fatty acids esters were carried out in a mechanically stirred 1.1 L stainless steel pressure reactor, equipped with a heating/cooling jacket supplied by a thermostat controlled by a thermocouple dipping into the reaction mixture. Prior to alkoxycarbonylation experiments the reactor was evacuated and purged with nitrogen several times.

Synthesis of Dimethyl-1,19-nonadecanedioate[14]

Methyl oleate (150 mL, Dakolub MB 9001) was dissolved in 500 mL of methanol and cannula transferred into the pressure reactor under a nitrogen atmosphere. A solution of the catalyst precursor [(dtbpx)Pd(OTf)$_2$] (687 mg, 0.86 mmol) in another 50 mL of methanol was added, and the reactor was pressurized with 20 bar of CO and heated to 90 °C. A constant CO pressure was maintained by periodic replenishing. After 120 h 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. Removal of the solvent *in vacuo* and recrystallization from methanol yielded pure dimethyl-1,19-nonadecanedioate (115.0 g, 76 %, purity 99.5 % from GC, confirmed by ^{1}H- and ^{13}C-NMR spectroscopy).



^{1}H-NMR (CDCl$_3$, 25 °C, 400 MHz): δ 3.66 (s, 6H, H-1), 2.30 (t, $^3J_{H\text{-}H}$ = 7.6 Hz, 4H, H-3), 1.67-1.56 (m, 4H, H-4), 1.35-1.20 (m, 26H, H-5).

^{13}C{^{1}H} NMR (CDCl$_3$, 25 °C, 101 MHz): δ 174.48 (s, C-2), 51.56 (s, C-1), 34.28 (s, C-3), 30.16-29.15 (C-5), 25.12 (s, C-4).

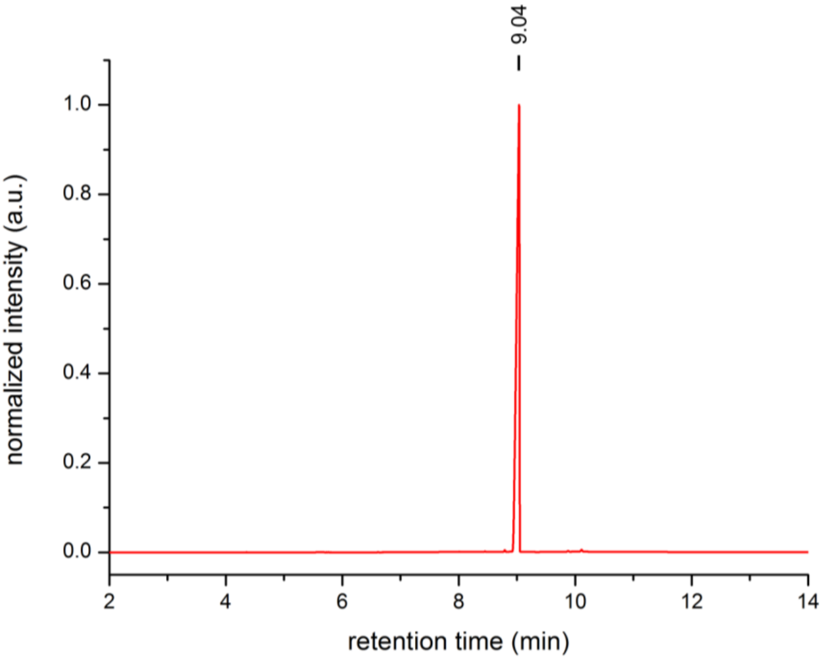
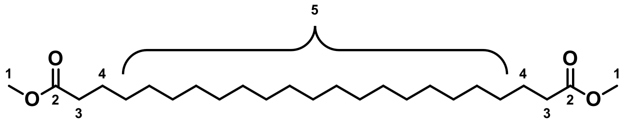


Figure 5.10: Gas chromatogram (1.0 min isothermal at 90 °C, 30 K min^{-1} to 280 °C, 8 min isothermal) of pure dimethyl-1,19-nonadecanedioate.

Synthesis of Dimethyl-1,23-tricosanedioate

Employing methyl erucate (175 mL) rather than methyl oleate in an otherwise identical procedure yielded pure dimethyl-1,23-tricosanedioate (96.0 g, 54 %, purity 99.6 % from GC, confirmed by ^{1}H and ^{13}C NMR spectroscopy).



^{1}H-NMR (CDCl$_3$, 25 °C, 400 MHz): δ 3.66 (s, 6H, H-1), 2.29 (t, $^3J_{H\text{-}H}$ = 7.6 Hz, 4H, H-3), 1.68-1.58 (m, 4H, H-4), 1.35-1.18 (m, 34H, H-5).

^{13}C{^{1}H} NMR (CDCl$_3$, 25 °C, 101 MHz): δ 174.45 (s, C-2), 51.55 (s, C-1), 34.27 (s, C-3), 30.18-29.13 (C-5), 25.12 (s, C-4).

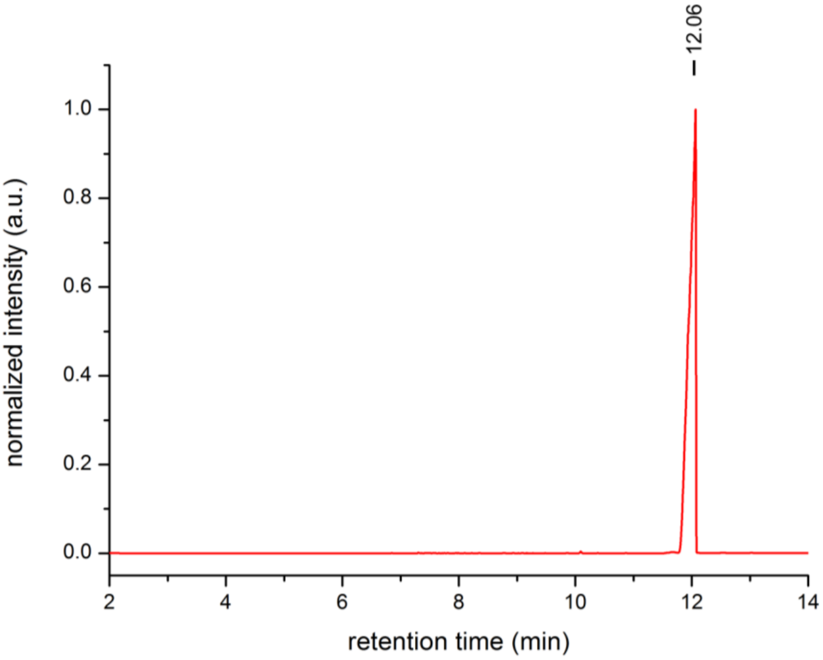


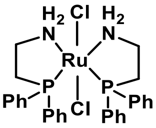
Figure 5.11: Gas chromatogram (1.0 min isothermal at 90 °C, 30 K min^{-1} to 280 °C, 8 min isothermal) of pure dimethyl-1,23-tricosanedioate.

Synthesis of Dichlorobis[2-(diphenylphosphino)ethylamine]ruthenium

Tris(triphenylphosphine)ruthenium(II) dichloride (419 mg; 0,436 mmol) was dissolved in 6 mL of toluene in a 100 mL round bottom flask and a solution of 2-(diphenylphosphino)ethylamine (202 mg; 0,879 mmol) in 6 mL toluene was added dropwise within one hour. After stirring the reaction mixture over night at room-temperature, the yellow suspension was washed several times with toluene until the filtrate was colorless. Removing the solvent *in vacuo* yielded the desired complex (298 mg, 77 %) as a pale-yellow solid.

$^{31}P\{^1H\}$ NMR analysis in accordance to literature[34] showed the presence of two species the major

one being the *trans-* chloride-*cis*-phosphorous complex and the minor one being the *cis*-chloride-*cis*-phosphorous complex.

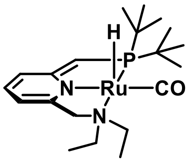


$^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C, 162 MHz): δ 61.92 (s; *trans-cis*-product); δ 67.26 (d, $^2J_{P-P}$ = 32 Hz) and 55.38 (d, $^2J_{P-P}$ = 32 Hz *cis-cis*-product)

Synthesis of Nonadecane-1,19-diol

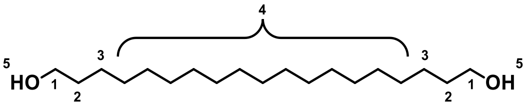
Catalytic reduction of the α,ω-diester was carried out, analogous to a reported procedure,[19] in a 300 mL stainless steel mechanically stirred pressure reactor equipped with a heating jacket and a glass inlay. Prior to the reduction experiment the reactor was purged several times with argon. Dimethyl-1,19-nonadecanedioate (33.6 mmol; 12.0 g) was weighed under air into a dry Schlenk tube equipped with a magnetic stir bar which was then purged several times with argon. 100 mL dry and degassed THF were added. Vigorous stirring afforded a homogenous reaction mixture. In the glovebox dichlorobis[2-(diphenylphosphino)ethylamine]ruthenium (33.6 μmol; 20 mg) and sodium methanolate (2.20 mmol; 120 mg) were weighed into a second dry Schlenk tube equipped with a magnetic stir bar. After removing the Schlenk tube from the glovebox, 100 mL dry and degassed THF were added. Both mixtures were then cannula-transferred into the reactor in an argon counter stream. The reactor was closed, pressurized with 50 bar hydrogen and then heated to 100 °C for 22 hours while stirring. After cooling down to room temperature the reactor was vented. The reaction mixture was retrieved from the reactor and heated to around 50 °C in order to remove catalyst residues by filtration over a Buchner funnel. Removing the solvent *in vacuo* and recrystallization from chloroform yielded nonadecane-1,19-diol (8.4 g, 83 %).

Alternatively catalytic reduction of dimethyl-1,19-nonadecanedioate is also possible using a ruthenium hydride complex based on the pincer ligand PNN (2-(di-*tert*-butylphosphinomethyl)-6-(diethylaminomethyl)pyridine), which was developed by Milstein and coworkers.[20]



For this purpose the α,ω-diester (2.0 mmol; 713 mg) is weighed into a Schlenk tube together with carbonylhydrido[6-(di-*tert*-butylphosphinomethylene)-2-(N,N-diethylaminomethyl)-1,6-dihydro-pyridine]ruthenium(II) (0.1 mmol; 50 mg). After addition of 10 mL dioxane the reaction mixture was transferred into the pressure reactor, which was pressurized with 10 bar H_2 and heated to

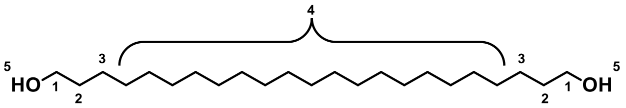
115 °C for 24 hours. ^{1}H-NMR of the crude reaction product after removing the solvent *in vacuo* showed virtually complete conversion to the desired diol component.



^{1}H-NMR ($CDCl_3$, 50 °C, 400 MHz): δ 3.64 (q, $^{3}J_{H\text{-}H}$ = 6.4 Hz, 4.9 Hz, 4H, H-1), 1.57 (quint, $^{3}J_{H\text{-}H}$ = 6.9 Hz, 4H, H-2), 1.45-1.24 (m, 30H, H-3 and H-4), 1.21 (t, $^{3}J_{H\text{-}H}$ = 4,9 Hz, 2H, H-5).
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 50 °C, 101 MHz): δ 63.22 (C-1), 33.03 (C-2), 29.99-29.60 (C-4), 25.94 (C-3).

Synthesis of Tricosane-1,23-diol

The reduction of dimethyl-1,23-tricosanedioate was carried out analogous to the procedure described above for its 1,19-analogue. After retrieving the reaction mixture from the reactor it was heated to around 50 °C and then filtrated over a Buchner funnel to remove catalyst residues. THF was removed *in vacuo*. Tricosane-1,23-diol was recrystallized from chloroform to obtain 78 % yield (9.3 g).



^{1}H NMR ($CDCl_3$, 50°C, 400 MHz): δ 3.64 (q, $^{3}J_{H\text{-}H}$ = 6.4 Hz, 4.9 Hz, 4H, H-1), 1.57 (quint, $^{3}J_{H\text{-}H}$ = 6.9 Hz, 4H, H-2), 1.45-1.24 (m, 38H, H-3 and H-4), 1.21 (t, $^{3}J_{H\text{-}H}$ = 5.1 Hz, 2H, H-5).
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 50 °C, 101 MHz): δ 63.29 (C-1), 33.08 (C-2), 29.96-29.52 (C-4), 25.96 (C-3).

5.4.3 Polycondensation

Polyesters were prepared in a 100 mL two-necked Schlenk tube equipped with an overhead stirrer. Efficient mixing of the highly viscous polymer melt was achieved by a helical agitator. Under a static argon atmosphere the monomers (20.0 mmol of dimethyl-1,19-nonadecanedioate or diethyl-1,23-tricosanedioate, respectively, and 20.0 mmol of the corresponding α,ω-diol) were filled into the reaction vessel and molten by heating to 120 °C. A 0.6 mL aliquot of a 0.028 M titanium(IV) butoxide solution in toluene was injected, and the temperature was raised to 200 °C over the course of 8 h. Finally, the polymer melt was stirred for about 16 h at this temperature under reduced pressure (0.01 mbar).

5.4.4 Rheological testing

Rheological measurements were carried out with an Advanced Rheometric Expansion System (ARES) from Rheometric Scientific at the Freiburg Materials Research Center together with

Benjamin Ritter. Test specimens (25 mm diameter) were prepared with a Dr. Collin vacuum press 200 PV at 180 °C, and a pressure of 30 bar was sustained for 30 minutes. Polymers were stabilized with 1 wt.-% of (±)-α-tocopherol. Specimens were analyzed using a plate/plate geometry (25 mm diameter). The frequency was varied between 0.1 and 100 rad s^{-1}. The temperature was raised from 110 to 180 °C during the measurement.

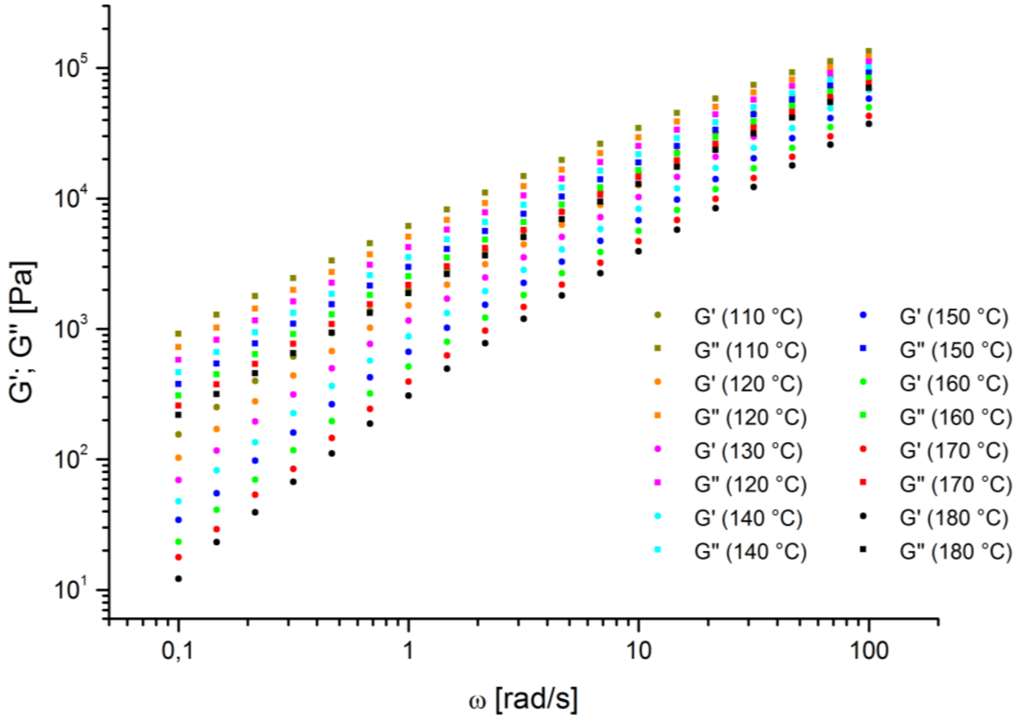


Figure 5.12: Isothermals of G` and G`` for rheological study of **PE-19.19** (gap = 0.5 mm).

In order to obtain the master curves the isotherms were shifted only in horizontal dimension (b_T = 1) at a reference temperature of T_0 = 150 °C using the following a_T-values:

Table 5.5: a_T-values of **PE-19.19**.

entry	temperature [K]	a_T value
1	383.1	2.727
2	393.1	2.075
3	403.1	1.607
4	413.1	1.266
5	423.1	1.000
6	433.1	0.803
7	443.1	0.655
8	453.1	0.522

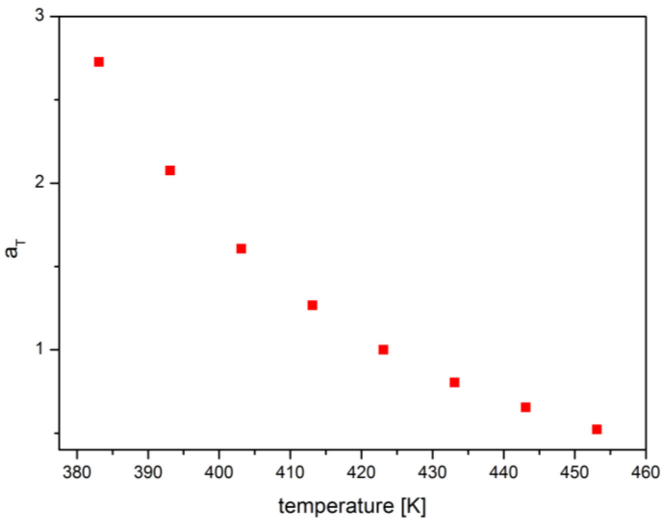


Figure 5.13: Temperature dependence of the a_T-values measured for **PE-19.19**.

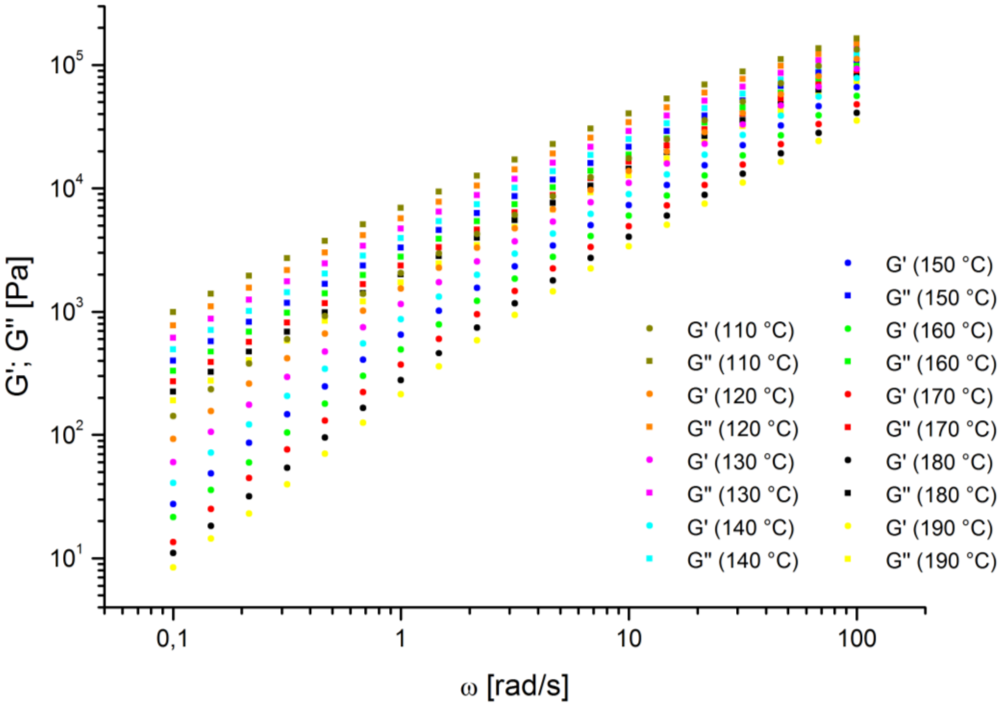


Figure 5.14: Isothermals of G` and G`` for rheological study of **PE-23.23** (gap = 0.5 mm).

In order to obtain the master curves the isotherms were shifted only in horizontal dimension (b_T = 1) at a reference temperature of T_0 = 150 °C using the following a_T-values:

Table 5.6: a_T-values of **PE-23.23**.

entry	temperature [K]	a_T value
1	383.1	2.650
2	393.1	2.035
3	403.1	1.581
4	413.1	1.251
5	423.1	1.000
6	433.1	0.812
7	443.1	0.660
8	453.1	0.544

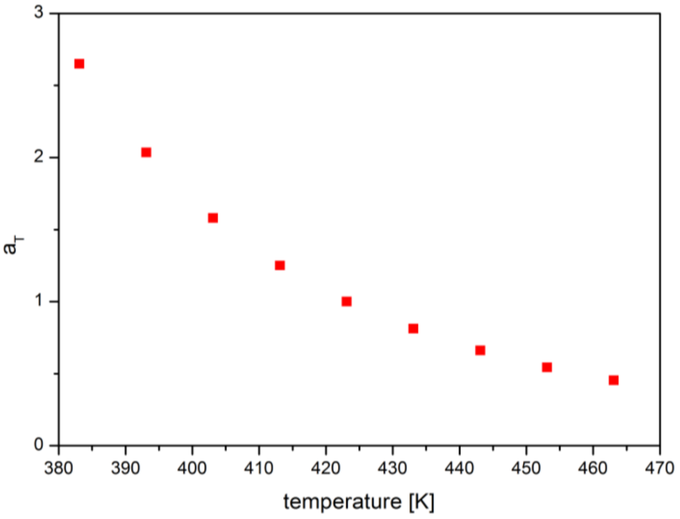


Figure 5.15: Temperature dependence of the a_T-values measured for **PE-23.23**.

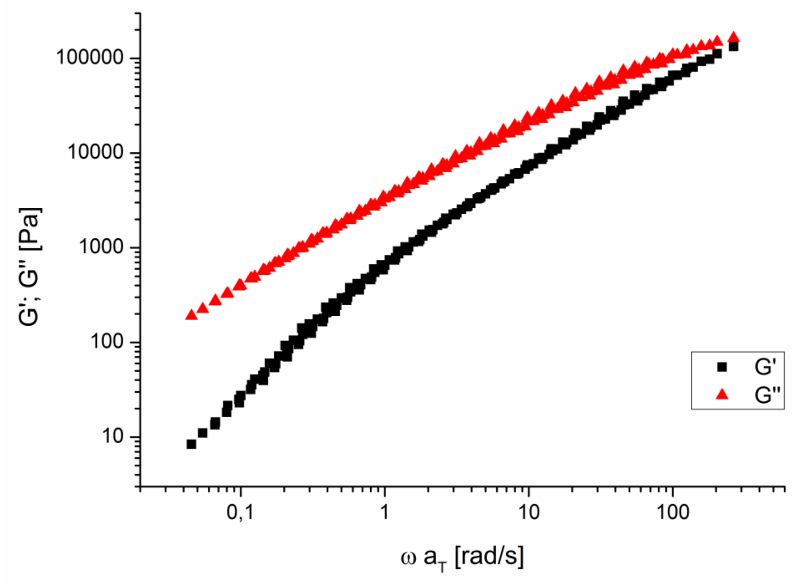


Figure 5.16: Master curves of G\` and G\`\` for **PE-23.23** (from measurements at 110, 120, 130, 140, 150, 160 and 180 °C). Shifting temperature is 150 °C.

To determine zero-shear viscosity from experimental data, the Carreau-Yasuda[35] equation is used:

$$\eta` = \frac{\eta_0}{(1 + a\omega^{\alpha})^{\beta}}$$

Were $\eta`$ stands for complex viscosity, η_o is zero-shear viscosity, with ω for frequency and a, α and β are fitting parameters. The values of parameters in Carreau-Yasuda equation for the studied samples are reported in **Table 5.7**.

Table 5.7: Fitted parameters for Carreau-Yasuda equation.

	a	**α**	**β**	**η_0 [Pa s]**
PE-19.19	355	3092	198	3717 ± 26
PE-23.23	979	3955	1189	4032 ± 24

5.4.5 Tensile testing

Tensile tests were carried out at the Freiburg Materials Research Center together with Benjamin Ritter. For this purpose, dogbone-shaped sample bars (75 × 12.5 × 2 mm^3; ISO 527-2, type 5A) were prepared via melt compounding at 180 °C and 150 rpm for 3 min, using a DSM Xplore Micro 5cc Twin Screw Compounder and a DSM Xplore Micro 4cc Injection Molding Machine. In order to prevent oxidative degradation the polymers were stabilized with 1 wt.-% of (±)-α-tocopherol.

After preconditioning the samples over night at 23 °C tensile tests were performed on Zwick Z005 instrument according to ISO 527 (crosshead speed 5.0 mm min^{-1}). The Zwick testXpert software version 11.0 was used to collect and analyze the results. Young's modulus, stress at yielding, strain at yielding, tensile stress at break and elongation at break were obtained by averaging the data from several test specimens.

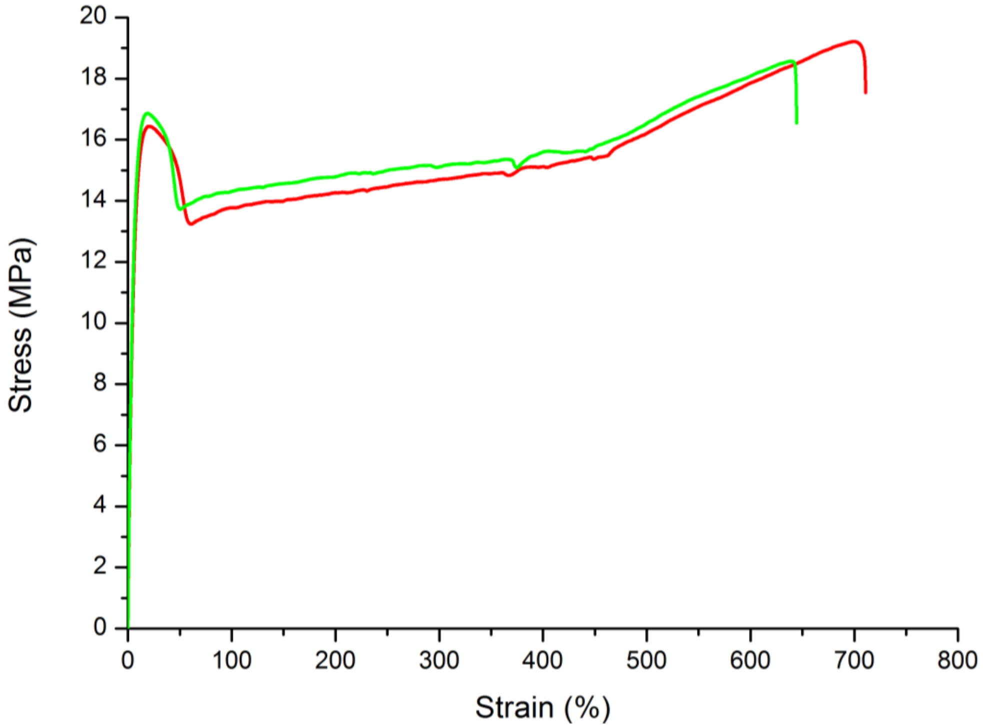


Figure 5.17: Stress-strain curves (constant drawing rate of 5.0 mm min^{-1}, room temperature) of **PE-23.23**.

5.4.6 Shore D hardness

Measuring Shore D Hardness (according DIN 535054) was performed with a Zwick 3150 H04 instrument at room temperature. For determination of hardness 12.5 × 12.5 × 4 mm^3 test specimens were used. Values given are the average of six independent measurements.

5.4.7 Dynamic mechanical analysis

Dynamic-mechanical analyses (DMA) were recorded on melt compounded rectangular specimens (length × width × thickness = 25 × 6 × 2 mm^3) using a Triton Technology TTDMA instrument equipped with single cantilever geometry. Measurements were performed from -150 °C to 80 °C at a heating rate of 3 °C min^{-1} and a frequency of 1 Hz. The Triton Technology DMA software was used to acquire and process the data. Glass transition temperatures (T_g) were determined from the temperature position of the maximum in loss modulus (G``).

For **PE-23.23** from the loss modulus *vs.* temperature a T_g of -27 °C was observed. The second relaxation phenomenon at around -130 °C can be ascribed to the motion of the methylene sequences of the polyester main-chain (**Figure 5.18**).

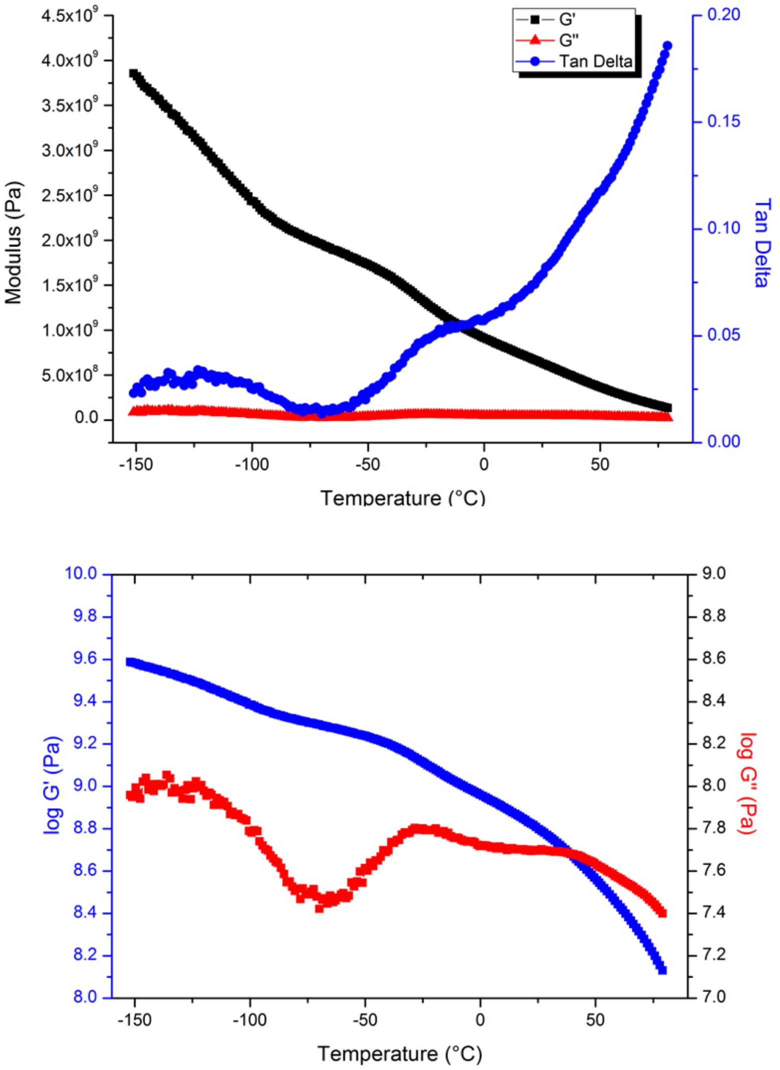


Figure 5.18: Dynamic mechanical analysis of **PE-23.23**.

5.4.8 Hydrolytic degradation

For the degradation experiments **PE-19.19** was extruded into a rectangular specimen (length × width × thickness = 25 × 6 × 2 mm^3) that was cut into 1 mm pieces. Hydrolytic degradation was studied by placing individual samples in 20 mL of PBS puffer (pH = 7.4), 20 wt.-% aq. NaOH, 1 M aq. HCl and concentrated aq. HCl at 40 °C. On a weekly basis the pellets were removed, washed with water and acetone and dried under vacuum for 24 h. After determination of the weight loss the media were renewed and the polymer samples were again exposed to their corresponding medium.

5.5 References

1. Oils and Fats as Renewable Raw Materials in Chemistry. Biermann, U.; Bornscheuer, U.; Meier, M. A. R.; Metzger, J. O.; Schäfer, H. J. *Angew. Chem. Int. Ed.* **2011**, *50*, 3854-3871.
2. Yamamoto, M.; Witt, U.; Skupin, G.; Beimborn, D.; Müller R.-J. in *Biopolymers*; Eds. Steinbüchel, A.; Doi, Y. Wiley-VCH: Weinheim, **2002**; Vol. 4, pp 299-311.
3. Lipid Biotechnology: Industrially Relevant Production Processes. Schörken, U.; Kempers, P. *Eur. J. Lipid Sci. Technol.* **2009**, *111*, 627-645.
4. Biocatalytic and Fermentative Production of α,ω-Bifunctional Polymer Precursors. Schaffer, S.; Haas, T. *Org. Process Res. Dev.* **2014**, *18*, 752-766.
5. High Turnover Numbers with Ruthenium-Based Metathesis Catalysts. Dinger, M. B.; Mol, J. C. *Adv. Synth. Catal.* **2002**, *344*, 671-677.
6. A General Model for Selectivity in Olefin Cross Metathesis. Chatterjee, A. K.; Choi, T.-L.; Sanders, D. P.; Grubbs, R. H. *J. Am. Chem. Soc.* **2003**, *125*, 11360-11370.
7. Metathesis of Unsaturated Fatty Acids: Synthesis of Long-Chain Unsaturated-α,ω-Dicarboxylic Acids. Ngo, H.; Jones, K.; Foglia, T. *J. Am. Oil Chem. Soc.* **2006**, *83*, 629-634.
8. Plant Oil-Based Long-Chain C_{26} Monomers and Their Polymers. Vilela, C.; Silvestre, A. J. D.; Meier, M. A. R. *Macromol. Chem. Phys.* **2012**, *213*, 2220-2227.
9. Which Polyesters Can Mimic Polyethylene? Stempfle, F.; Ortmann, P.; Mecking, S. *Macromol. Rapid Commun.* **2013**, *34*, 47-50.
10. Methods of Refining and Producing Fuel from Natural Oil Feedstocks. Cohen, S. A.; Luetkens, M. L.; Balakrishnan, C.; Snyder, R. (Elevance Renewable Sciences), WO 2011/046872 (A2), **2011**.
11. Press release by Elevance Renewable Sciences of July 18, 2013.
12. Refining of Plant Oils to Chemicals by Olefin Metathesis. Chikkali, S.; Mecking, S. *Angew. Chem. Int. Ed.* **2012**, *51*, 5802-5808.
13. Dicarboxylic Acid Esters from the Carbonylation of Unsaturated Esters under Mild Conditions. Jiménez-Rodriguez, C.; Eastham, G. R.; Cole-Hamilton, D. J. *Inorg. Chem. Commun.* **2005**, *8*, 878-881.
14. Linear Semicrystalline Polyesters from Fatty Acids by Complete Feedstock Molecule Utilization. Quinzler, D.; Mecking, S. *Angew. Chem. Int. Ed.* **2010**, *49*, 4306-4308.
15. Long-Chain Linear C_{19} and C_{23} Monomers and Polycondensates from Unsaturated Fatty Acid Esters. Stempfle, F.; Quinzler, D.; Heckler, I.; Mecking, S. *Macromolecules* **2011**, *44*, 4159-4166.

16. Mechanistic Features of Isomerizing Alkoxycarbonylation of Methyl Oleate. Roesle, P.; Dürr, C. J.; Möller, H. M.; Cavallo, L.; Caporaso, L.; Mecking, S. *J. Am. Chem. Soc.* **2012**, *134*, 17696-17703.
17. α,ω-Functionalized C_{19} Monomers. Walther, G.; Deutsch, J.; Martin, A.; Baumann, F.-E.; Fridag, D.; Franke, R.; Köckritz, A. *ChemSusChem* **2011**, *4* , 1052-1054.
18. Polymer Precursors from Catalytic Reactions of Natural Oils. Furst, M. R. L.; Goff, R. L.; Quinzler, D.; Mecking, S.; Botting, C. H.; Cole-Hamilton, D. J. *Green Chem.* **2012**, *14*, 472-477.
19. Dihydrogen Reduction of Carboxylic Esters to Alcohols under the Catalysis of Homogeneous Ruthenium Complexes: High Efficiency and Unprecedented Chemoselectivity. Saudan, L. A.; Saudan, C. M.; Debieux, C.; Wyss, P. *Angew. Chem. Int. Ed.* **2007**, *46*, 7473-7476.
20. Efficient Homogeneous Catalytic Hydrogenation of Esters to Alcohols. Zhang, J.; Leitus, G.; Ben-David, Y.; Milstein, D. *Angew. Chem. Int. Ed.* **2006**, *45*, 1113-1115.
21. a) Fermentative Herstellung der α,ω-Dicarbonsäure 1,18-Oktadecendisäure als Grundbaustein für Biobasierte Kunststoffe. Zibek, S.; Wagner, W.; Hirth, T.; Rupp, S.; Huf, S. *Chem. Ing. Tech.* **2009**, *81*, 1797-1808. b) Lipid Biotechnology: Industrially Relevant Production Processes. Schörken, U.; Kempers, P. *Eur. J. Lipid Sci. Technol.* **2009**, *111*, 627-645. c) Biotechnological Synthesis of Long-Chain Dicarboxylic Acids as Building Blocks for Polymers. Huf, S.; Krügener, S.; Hirth, T.; Rupp, S.; Zibek, S. *Eur. J. Lipid Sci. Technol.* **2011**, *113*, 548-561.
22. Hiemenz, P. C.; Lodge, T. P. *Polymer Chemistry, 2nd ed.*; CRC Press: Boca Raton, FL, **2007**.
23. Ward, I. M.; Sweeney, J. *Mechanical Properties of Solid Polymers*, Wiley, Chichester, 3rd Edn., 2012.
24. Effects of Molecular Weight on Poly(ω-pentadecalactone) Mechanical and Thermal Properties. Cai, J.; Liu, C.; Cai, M.; Zhu, J.; Zuo, F.; Hsiao, B. S.; Gross, R. A. *Polymer* **2010**, *51*, 1088-1099.
25. Catalytic Ring-Opening Polymerization of Renewable Macrolactones to High Molecular Weight Polyethylene-like Polymers. Van der Meulen, I.; Gubbels, E.; Huijser, S.; Sablong, R. l.; Koning, C. E.; Heise, A.; Duchateau, R. *Macromolecules* **2011**, *44*, 4301-4305.
26. For fibers cf.: Performance Polymers from Renewable Monomers: High Molecular Weight Poly(pentadecalactone) for Fiber Applications. De Geus, M.; van der Meulen, I.; Goderis, B.; van Hecke, K.; Dorschu, M.; van der Werff, H.; Koning, C. E.; Heise, A. *Polym. Chem.* **2010**, *1*, 525-533.

27. Polymers from Fatty Acids: Poly(ω-hydroxyl tetradecanoic acid) Synthesis and Physico-Mechanical Studies. Liu, C.; Liu, F.; Cai, J.; Xie, W.; Long, T. E.; Turner, S. R.; Lyons, A.; Gross, R. A. *Biomacromolecules* **2011**, *12*, 3291-3298.
28. Whiteley, K. S.; Heggs, T. G.; Koch, H.; Mawer, R. L.; Immel, W. Polyolefins. in *Ullmann's Encyclopedia of Industrial Chemistry*, *Vol. 14* (Eds: Gerhartz, W.; Elver, B.), Wiley-VCH, Weinheim, **2005**, pp. 1-103.
29. For example Hostalen GC 7260 (LyondellBasell) according to the suppliers data sheet exhibits a shore D hardness of 61.
30. The Glass Transition Temperature in Homologous Series of Linear Polymers. Grieveson, B. M. *Polymer* **1960**, *1*, 499-512.
31. The Relationship between Chemical Structure and Viscoelastic Properties of Linear Aliphatic Polyesters. Ito, M.; Kubo, M.; Tsuruta, A.; Tanaka, K. *J. Polym. Sci.: Polym. Phys. Ed.*, **1978**, *16*, 1435-1446.
32. Physical Characterization of Poly(ω-pentadecalactone) Synthesized by Lipase-Catalyzed Ring-Opening Polymerization. Letizia Focarete, M.; Scandola, M.; Kumar, A.; Gross, R. A. *J. Polym. Sci. Part B: Polym. Phys.*, **2001**, *39*, 1721-1729.
33. Polymers from Functional Macrolactones as Potential Biomaterials: Enzymatic Ring Opening Polymerization, Biodegradation, and Biocompatibility. Van der Meulen, I.; de Geus, M.; Antheunis, H.; Deumens, R.; Joosten, E. A. J.; Koning, C. E.; Heise, A. *Biomacromolecules* **2008**, *9*, 3404-3410.
34. Hydrogenation of Esters with Ru/bidentate Ligands Complexes. Saudan, L.; Dupau, P.; Riedhauser, J.-J.; Wyss, P.; U.S. Patent 7,763,758 (B2), **2010**.
35. Rouse Chains with Excluded Volume Interactions in Steady Simple Shear Flow. Prakash, J. R. *J. Rheol.,* **2002**, *46*, 1353-1380.

6 Thermoplastic polyester elastomers based on long-chain crystallizable aliphatic hard segments

6.1 Introduction

Thermoplastic elastomers (TPEs) combine the processing and recyclable characteristics of thermoplastics with the flexibility and ductility of elastomers.[1] They have found widespread applications in e.g. electronics, clothing, adhesives and automotive components. Unlike classical vulcanized rubbers they do not possess permanent chemical, but reversible physical crosslinks via crystallites. At sufficiently high temperatures these physical forces can be disrupted and the TPEs become (re)processable, which can also allow for recycling or reuse. Morphologically, most TPEs are multiphase systems, with one or more types of hard phases and an elastomeric soft phase (**Figure 6.1**).

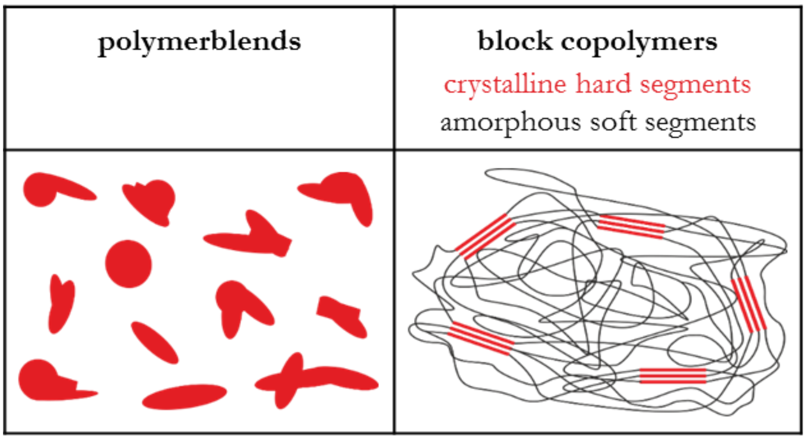


Figure 6.1: Schematic representation of TPEs' phase structure.

Besides blending one possible approach to obtain such microstructures is block copolymerization. Widely used representatives of such block copolymers are styrenic ABA triblock copolymers, such as poly(styrene-*b*-butadiene-*b*-styrene) (SBS) or poly(styrene-*b*-isoprene-*b*-styrene) (SIS) from anionic polymerizations.[2] Recently, analogues based partly or entirely on renewable feedstocks have also been developed.[3] Additionally, AB diblock or ABA triblock copolymers can be synthesized using atom transfer radical polymerization (ATRP).[4] In all these approaches polymerizations are performed in a sequential manner, adding a second monomer after one block has been grown. However, TPEs can also be generated by chain growth polymerization in a single step as illustrated by multiblock copolymers obtained via chain-shuttling ethylene/1-olefin insertion polymerizations.[5,6]

TPEs are also accessible via classical step-growth polymerization of difunctional monomers. For example, thermoplastic polyester elastomers consisting of amorphous poly(tetramethylene glycol) soft phases and crystalline poly(butylene terephthalate) hard segments are applied widely.[7] In these TPEs physical crosslinking is provided by crystallizable aromatic polyester hard segments. A utilization of aliphatic hard segments in such polycondensates - that is exploiting polyethylene-like crystallinity for physical cross-linking - has been prohibited by a lack of access to the required monomers. However, as further outlined in the previous chapters α,ω-difunctional linear long-chain compounds have recently become available from common seed oils via biotechnological[8] or chemical catalytic routes such as metathesis[9] or isomerizing alkoxycarbonylation.[10] The long methylene sequences originating from complete incorporation of the entire fatty acid chain in these monomers impart a polyethylene-like solid state structure in all-aliphatic polyesters discussed in the previous chapters and also in polycarbonates and polyacetals.[11] Here, the utility of such long-chain aliphatic dicarboxylic acids and diols for the generation of all-aliphatic thermoplastic polyester elastomers is demonstrated.

6.2 Results and discussion

6.2.1 Syntheses of thermoplastic polyester elastomers based on aliphatic hard segments

For the synthesis of thermoplastic polyester elastomers erucic acid-based dimethyl-1,23-tricosanedioate was employed, together with 1,23-tricosanediol, generated from the former via catalytic hydrogenation, as aliphatic hard segment. Dihydroxy-terminated poly(tetramethylene glycol) (PTMG) served as diol macromonomer for the generation of soft blocks. Molecular weights of the copolymers obtained amount to M_n 3 to 6 × 10^4 g mol^{-1} according to end group analysis from ^1H NMR spectroscopy. This is qualitatively confirmed by GPC analysis which also shows well behaved molecular weight distribution M_w/M_n around 2 (**Table 6.1**). Note that apparent GPC molecular weight *vs.* polystyrene standards used here typically overestimate molecular weights for polymers with hydrocarbon segments.

Table 6.1: Polyester-polyether copolymers based on long-chain crystallizable hard segments.

	sample	diacid	diol (1)	diol (2)	$M_{n,NMR}$[a] [g mol^{-1}]	$M_{n,GPC}$[b] [g mol^{-1}]	M_w/M_n[b]	T_m[c] [°C]	T_c[c] [°C]
1	TPE-$C_{23}PTMG_{1000}$-73wt.-%	4 (C_{23})	4 ($PTMG_{1000}$)		3.8×10^4	10.9×10^4	1.9	40	7/23
2	TPE-$C_{23}PTMG_{1000}$-62wt.-%	4 (C_{23})	3 ($PTMG_{1000}$)	1 (C_{23})	5.0×10^4	11.1×10^4	2.3	44/68[d]	24/47[d]
3	TPE-$C_{23}PTMG_{1000}$-48wt.-%	4 (C_{23})	2 ($PTMG_{1000}$)	2 (C_{23})	3.4×10^4	10.9×10^4	1.9	87	66
4	TPE-$C_{23}PTMG_{1000}$-29wt.-%	4 (C_{23})	1 ($PTMG_{1000}$)	3 (C_{23})	5.1×10^4	n.d.	n.d.	96	74
5	TPE-$C_{23}PTMG_{2000}$-85wt.-%	4 (C_{23})	4 ($PTMG_{2000}$)		4.1×10^4	12.6×10^4	1.9	34	7
6	TPE-$C_{23}PTMG_{2000}$-77wt.-%	4 (C_{23})	3 ($PTMG_{2000}$)	1 (C_{23})	4.0×10^4	8.9×10^4	1.9	30/63[d]	3/37[d]
7	TPE-$C_{23}PTMG_{2000}$-65wt.-%	4 (C_{23})	2 ($PTMG_{2000}$)	2 (C_{23})	3.8×10^4	11.4×10^4	2.0	23/86[d]	-3/64[d]
8	TPE-$C_{23}PTMG_{2000}$-45wt.-%	4 (C_{23})	1 ($PTMG_{2000}$)	3 (C_{23})	5.6×10^4	n.d.	n.d.	93	71

a) Determined by end-group analysis from ^1H-NMR spectroscopy. b) Determined by GPC in THF at 50 °C *vs.* polystyrene standards. c) Determined by DSC with a heating/cooling rate of 10 K min^{-1}. d) Broad melting and crystallization transitions are observed.

Polycondensation of stoichiometric amounts of dimethyl-1,23-trisocanedioate together with only di-hydroxy terminated poly(tetramethylene glycol) (PTMG) as a 'soft' diol component, yields polyester-polyether copolymers with low melting temperatures of about 40 °C for PTMG with a number average molecular weight of about 1000 g mol^{-1} ($PTMG_{1000}$) and 34 °C for the corresponding polycondensate with $PTMG_{2000}$ (**Table 6.1**, entries 1 and 5. The content of the soft diol in these polymers is 73 and 85 wt.-%, respectively). The thermal properties of these polymers basically reflect the polyether soft phase as the number of methylene units of the long-chain dicarboxylic component alone is not sufficient to provide significant crystalline domains. In order to increase the portion of the crystalline hard phase, the polyether diol macromonomer was partially replaced for the long-chain aliphatic diol, resulting in significantly increased melt and crystallization temperatures with increasing content of 1,23-tricosanediol (**Table 6.1**).

The DSC thermograms obtained for these polymers feature an additional melt peak for the crystalline hard segments, which dominates entirely at a content of the 'soft' polyether-diol of less than ca. 65 wt.-% (**Figure 6.2 and Figure 6.7**). This peak melting temperature of the hard segment (63 °C to 96 °C) is depressed with increasing polyether content. Such a behavior is also observed for TPEs based on crystalline poly(butylene terephthalate) hard segments and poly-(tetramethylene glycol) soft phases[12] and can be attributed to the larger amount of crystal imperfections due to the altered microstructure and the consequent less favorable crystallization conditions.

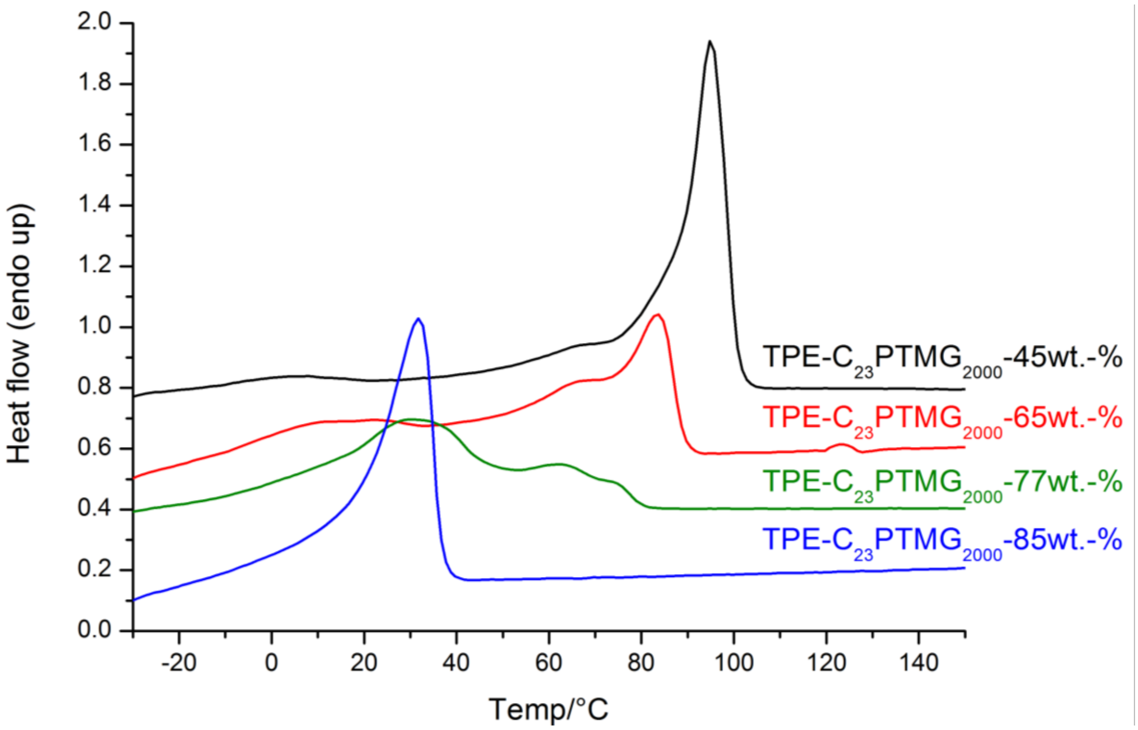


Figure 6.2: DSC thermograms (second heat) of polyester-polyether copolymers based on $PTMG_{2000}$.

By comparison to polyester-polyether copolymers based on the commercially available shorter chain dodecanedioic acid thermal properties are significantly enhanced. DSC analysis of TPE-$C_{12}PTMG_{1000}$-63wt.-% and TPE-$C_{12}PTMG_{2000}$-62wt.-% showed melting points of 52 °C and 66 °C, respectively, that is 20 °C lower than for their long-chain analogues at comparable co-polyester mass compositions and chain lengths of the polyether segments (1000 *vs.* 2000 g mol^{-1}) (**Table 6.1** and **Table 6.4**). This can be attributed to a lowering of the cohesion energy by additional ester groups incorporated in the crystalline domains, and larger amount of crystal imperfections caused by the additional ester groups interrupting the crystallizable hydrocarbon chains of the hard segments and the consequent less favorable crystallization conditions.

6.2.2 Mechanical properties of thermoplastic polyester elastomers based on aliphatic hard segments

First tensile tests on polyester-polyether copolymers were performed on dogbone-shaped test specimens prepared by piston injection molding (cf. Experimental section). Polymers with relatively low contents of the soft polyether phase behave like semi-rigid thermoplastics, with limited elongation at break (ε_b < 200 %) and irreversible deformation (**Table 6.2**, entry 4 with 29 wt.-% of $PTMG_{1000}$). However, at higher contents elastomeric behavior is observed, with satisfactory recovery and an elongation at break up to 870 %. Young moduli generally decrease with an increasing content of polyether soft segment for all polymer series, as expected (cf. **Table 6.2**).

Table 6.2: Mechanical properties of polyester-polyether copolymers based on long-chain crystallizable hard segments

	sample	diacid	diol (1)	diol (2)	Young's modulus[a,b] [MPa]	Elongation at break[a] [%]	Permanent set[c] [%]
1	TPE-$C_{23}PTMG_{1000}$-73wt.-%	4 (C_{23})	4 ($PTMG_{1000}$)		n.d.	n.d.	n.d.
2	TPE-$C_{23}PTMG_{1000}$-62wt.-%	4 (C_{23})	3 ($PTMG_{1000}$)	1 (C_{23})	60	220	45
3	TPE-$C_{23}PTMG_{1000}$-48wt.-%	4 (C_{23})	2 ($PTMG_{1000}$)	2 (C_{23})	96	410	41
4	TPE-$C_{23}PTMG_{1000}$-29wt.-%	4 (C_{23})	1 ($PTMG_{1000}$)	3 (C_{23})	122	170	100
5	TPE-$C_{23}PTMG_{2000}$-85wt.-%	4 (C_{23})	4 ($PTMG_{2000}$)		n.d.	n.d.	n.d.
6	TPE-$C_{23}PTMG_{2000}$-77wt.-%	4 (C_{23})	3 ($PTMG_{2000}$)	1 (C_{23})	34	630	36
7	TPE-$C_{23}PTMG_{2000}$-65wt.-%	4 (C_{23})	2 ($PTMG_{2000}$)	2 (C_{23})	38	874	30
8	TPE-$C_{23}PTMG_{2000}$-45wt.-%	4 (C_{23})	1 ($PTMG_{2000}$)	3 (C_{23})	78	290	45

a) Tensile tests according to ISO 527/1-2, specimen type 5A prepared by injection molding. b) Crosshead speed 1 mm min^{-1}. c) Determined from hysteresis experiments after 10 cycles at an elongation of 100 % with a constant crosshead speed of 50 mm min^{-1}.

In order to assess the elastic properties of these new materials preliminary shape recovery tests were performed. For this purpose melt compounded rectangular specimens (length × width × thickness = $60 \times 10 \times 1$ mm^3) were repeatedly exposed to a constant stress of about 5.6 MPa or extended to a defined strain of ca. 80 % (**Figure 6.3**).

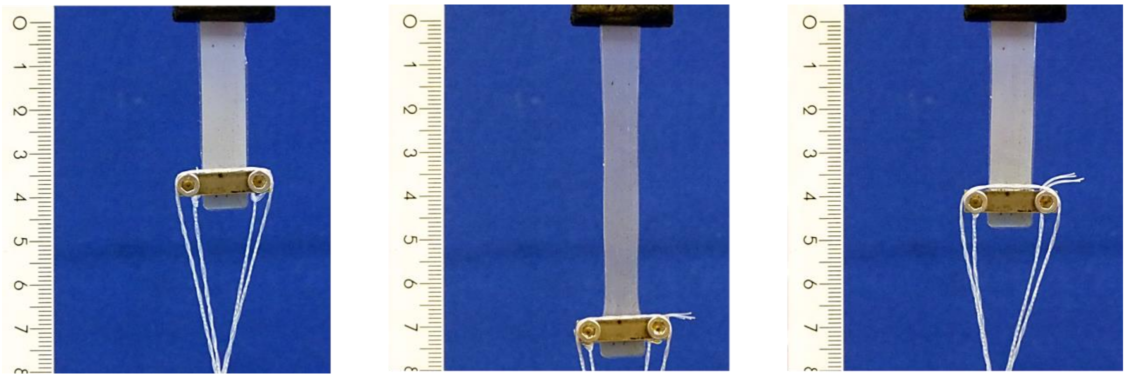


Figure 6.3: Shape recovery tests of polyester-polyether copolymer TPE-C$_{23}$PTMG$_{2000}$-65wt.-%.

Cyclic repetition of these loading and unloading experiments up to 100 cycles clearly demonstrate, that after the first few cycles, where the residual deformation gradually increases, an almost constant level of recovery is reached as exemplified here for TPE-C$_{23}$PTMG$_{2000}$-65wt.-% (**Figure 6.4**). This behavior is typical for TPEs[1] and can be ascribed to the alignment of the polymer microstructure.[13] After an initial change in morphology, a largely constant structure is adopted and hysteresis is observed (providing the repeated deformation is kept on the same order).

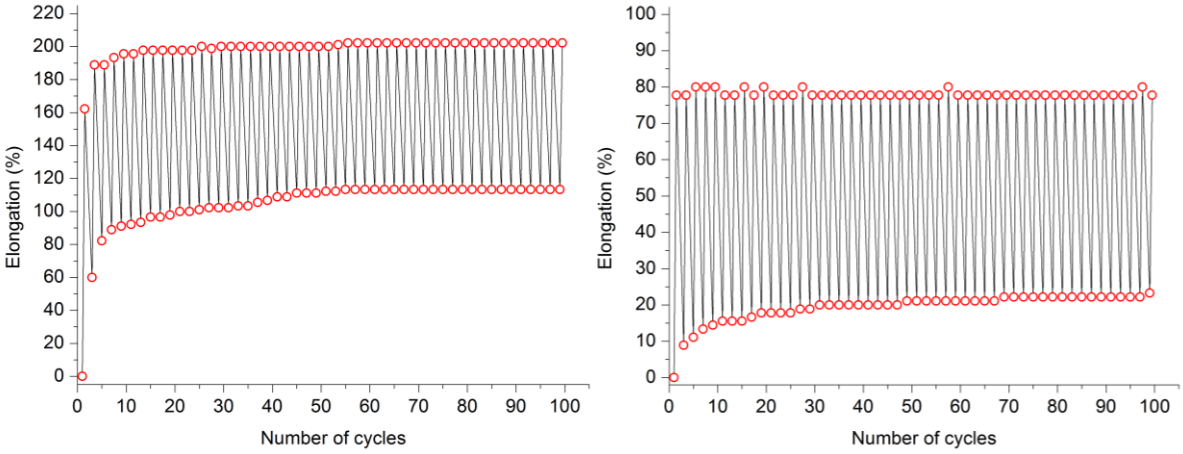


Figure 6.4: Shape recovery tests on polyester-polyether copolymer TPE-C$_{23}$PTMG$_{2000}$-65wt.-% applying constant stress of about 5.6 MPa (left) and a constant strain of ca. 80 % (right) (for clarity only every second cycle is displayed).

These preliminary results were further confirmed by cyclic hysteresis tests on dogbone-shaped sample bars, which were repeatedly exposed to consecutive cycles of loading and unloading to a constant strain of 100 % in a tensile testing machine.

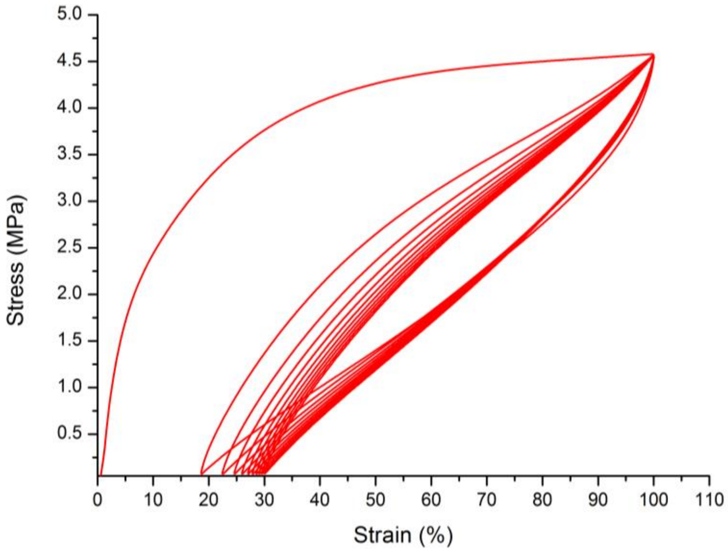


Figure 6.5: Stress-strain curves from cyclic tensile tests with a constant strain of 100 % for polyester-polyether copolymer TPE-$C_{23}PTMG_{2000}$-65wt.-% (10 cycles are displayed).

Again, upon cyclic repetition with up to 100 cycles, after the first few cycles, where the residual deformation gradually increases, all the TPEs studied here exhibit a virtually constant level of recovery. After 10 cycles this residual strain ranges between 30 % and 45 % (**Table 6.2**). Polyester-polyether copolymers containing polyether segments with a number average molecular weight of 2000 g mol^{-1} show better elastomeric behavior than the corresponding copolymers with polyether segments of 1000 g mol^{-1}. For both series, copolymers with 50 mol-% of polyether soft diol exhibit the smallest residual strain, indicating this to be an optimum ratio of hard and soft segment (cf. **Figure 6.5**, **Figure 6.10** and **Table 6.2**, entry 3 and 7).

In order to further investigate the effect of the long hydrocarbon chain of the aliphatic hard segments, polyester-polyether copolymers based on the mid-chain aliphatic monomers dodecanedioic acid and dodecanediol with a comparable weight fraction of polyether diols were prepared. Considering their chain microstructures, the most relevant difference will be that the shortest ‘hard block’, i.e. an isolated diacid repeat unit, is already twice as large for the long-chain monomer based polyester (C_{23}) *vs.* its mid-chain analogue (C_{12}). A statistical consideration of block length distributions (**Figure 6.6**, comparing C_{24} and C_{12} spaced polymers for the sake of clarity) shows that these constitute only a relatively small portion of the aliphatic blocks in the polymer composition discussed. Overall, block length distributions are similar at the polymer composition of interest, apart from a slightly higher heterogeneity of the mid-chain polyester due to the larger range of block length relevant here.

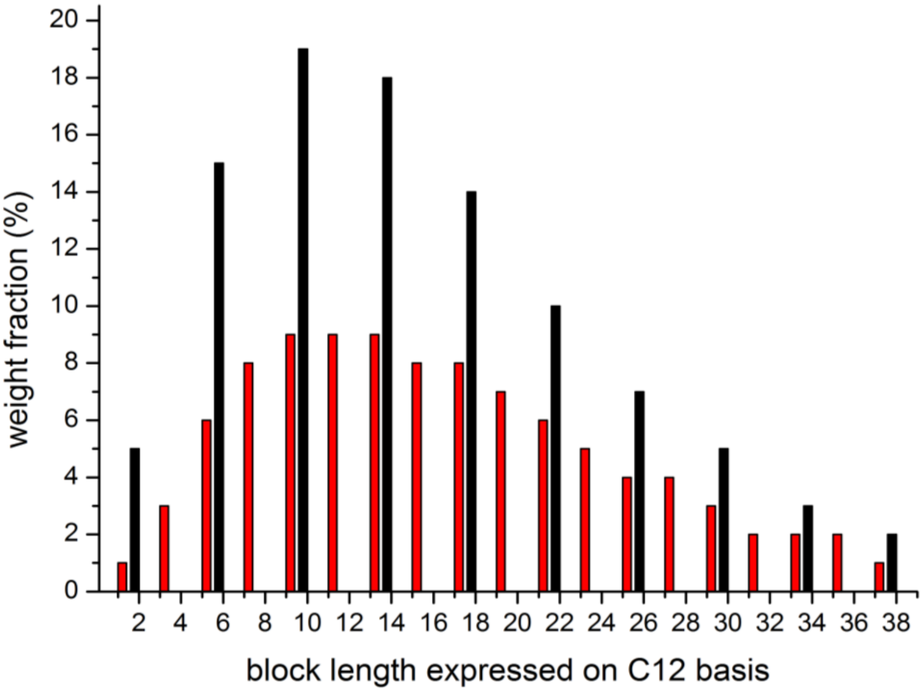


Figure 6.6: Block lengths distributions expressed on C_{12}-basis for copolyester of C_{24} dicarboxylic acid with C_{24} diol and 25 mol-% polyether (black) and for copolyester of C_{12} dicarboxylic acid with C_{12} diol and 14.3 mol-% polyether (red), i.e. isolated acid repeat unit: n = 1 (C_{12}) and n = 2 (C_{24}); acid- aliph. diol-acid: n = 3 (C_{12}) and n = 6 (C_{24}) etc.

Mechanical analysis of TPE-C_{12}PTMG$_{2000}$-62wt.-% for example showed that the lower chain-length of the monomers for the aliphatic hard segment does not result in dramatically different mechanical properties. TPE-C_{12}PTMG$_{2000}$-62wt.-% exhibited a slightly lower residual strain of 25 % and slightly higher Young's modulus (42 MPa) as well as elongation at break (880 %) than TPE-C_{23}PTMG$_{2000}$-62wt.-%. Furthermore it could be demonstrated that general trends observed for the mechanical properties of polyester-polyether copolymers based on the long-chain aliphatic hard segments can be also found in the series of their dodecanedioic acid/dodecanediol based analogues (**Table 6.3**).

Table 6.3: Mechanical properties of polyester-polyether copolymers based on dodecanedioic acid and dodecanediol hard segments

	sample	diacid	diol (1)	diol (2)	Young's modulus^{a,b} [MPa]	Elongation at break^{a} [%]	Permanent set^{c} [%]
1	TPE-C_{12}PTMG$_{2000}$-91wt.-%	4 (C_{12})	4 (PTMG$_{2000}$)		n.d.	n.d.	n.d.
2	TPE-C_{12}PTMG$_{2000}$-77wt.-%	4 (C_{12})	2 (PTMG$_{2000}$)	2 (C_{12})	7	840	35
3[14]	TPE-C_{12}PTMG$_{2000}$-62wt.-%	7 (C_{12})	2 (PTMG$_{2000}$)	5 (C_{12})	42	880	25

a) Tensile tests according to ISO 527/1-2, specimen type 5A prepared by injection molding. b) Crosshead speed 1 mm min^{-1}. c) Determined from hysteresis experiments after 10 cycles at an elongation of 100% with a constant crosshead speed of 50 mm min^{-1}.

6.3 Conclusion

By contrast to commercially available thermoplastic elastomers, where physical crosslinking is typically provided by crystallizable aromatic polyester hard segments, here the utility of plant-oil derived long-chain aliphatic dicarboxylic acids and diols for the generation of novel all-aliphatic thermoplastic polyester elastomers is demonstrated. Soft segments of these new materials are based on diol-terminated poly(tetramethylene glycol), which is also accessible from renewable (carbohydrate) feedstocks.[15] Polycondensation of these bio-based monomers yields polyester-polyether copolymers with molecular weights up to M_n 6×10^4 g mol^{-1}. Exploiting the poly-ethylene-like crystallinity, the long-chain aliphatic segments provide physical crosslinking that imparts elastomeric behavior to these thermoplastic materials. A particularly high recovery was observed at ca. 65 wt.-% (50 mol-% of the total diols employed) of PTMG$_{2000}$ soft segments. Compared to mid-chain analogues based on C$_{12}$ aliphatic monomers, melting points are significantly enhanced. DSC analysis of TPE-C$_{23}$PTMG$_{1000}$-62wt.-% and TPE-C$_{23}$PTMG$_{2000}$-65wt.-% showed melting points of 68 °C and 86 °C, respectively, that is ca. 20 °C higher than for their mid-chain analogues at comparable copolyester mass compositions and chain lengths of the polyether segments (1000 *vs.* 2000 g mol^{-1}). This is practically relevant, as the latter materials based on traditional mid-chain monomers appear prone to a softening and loss of their elastomeric properties upon temperature variations within ambient conditions.

6.4 Experimental section

6.4.1 Materials and general considerations

Toluene was distilled from sodium under an inert gas atmosphere. Titanium(IV) tetrabutoxide was supplied by Sigma-Aldrich and *N,N′*-di-2-naphthyl-1,4-phenylenediamine (> 96 %) was purchased from TCI Europe. Poly(tetramethylene glycol) with a number average molecular mass of M_n = 1000 purchased from Sigma-Aldrich and poly(tetramethylene glycol) with a number average molecular mass of M_n = 2000 kindly donated by BASF SE were all molten at 40 °C and degassed prior to use. Dimethyl-1,23-tricosanedioate[11b] and tricosane-1,23-diol[11b] were prepared from ethyl erucate according to previously reported literature procedures.

NMR spectra were recorded on a Varian Inova 400, a Bruker Avance 400 and on a Bruker Avance DRX 600 spectrometer. ^{1}H and ^{13}C chemical shifts were referenced to the solvent signals. High-temperature NMR measurements of polymers were performed in 1,1,2,2-tetrachloroethane-*d2* at 130 °C. Acquired data was processed and analysed using MestReNova software.

DSC analyses were performed on a Netzsch Phoenix 204 F1 instrument with a heating and cooling rate, respectively, of 10 K min^{-1} in a temperature range of -50 to 160 °C. Data reported are from second heating cycles.

Gel permeation chromatography (GPC) measurements were carried out on a Polymer Laboratories PL-GPC 50 with two PLgel 5 µm MIXED-C columns in THF at 50 °C against polystyrene standards with refractive index detection.

6.4.2 General polymerization procedure

Polycondensations were performed under an inert gas atmosphere in a 100 mL two-necked Schlenk tube, heated with an aluminium block. The temperature was controlled by a thermocouple in the block. The polymerization mixture was mechanically stirred by a helical agitator described in more detail in chapter 5.2.1. After weighing the desired amount of monomers (the amount of dimethyl-1,23-tricosanedioate was set to 10 mmol) and 0.05 mol-% of *N,N′*-di-2-naphthyl-1,4-phenylenediamine, the mixture was degassed and heated to 120 °C. Then, 0.6 mL of a 0.028 M solution of $Ti(OBu)_4$ in toluene was added and the temperature was increased by 10 K every 45 minutes. At a temperature of 180 °C vacuum was applied to remove volatiles. The mixture was then stirred overnight at 200 °C under vacuum. The resulting polyester-polyether copolymers were analysed by ^{1}H NMR, GPC and DSC measurements.

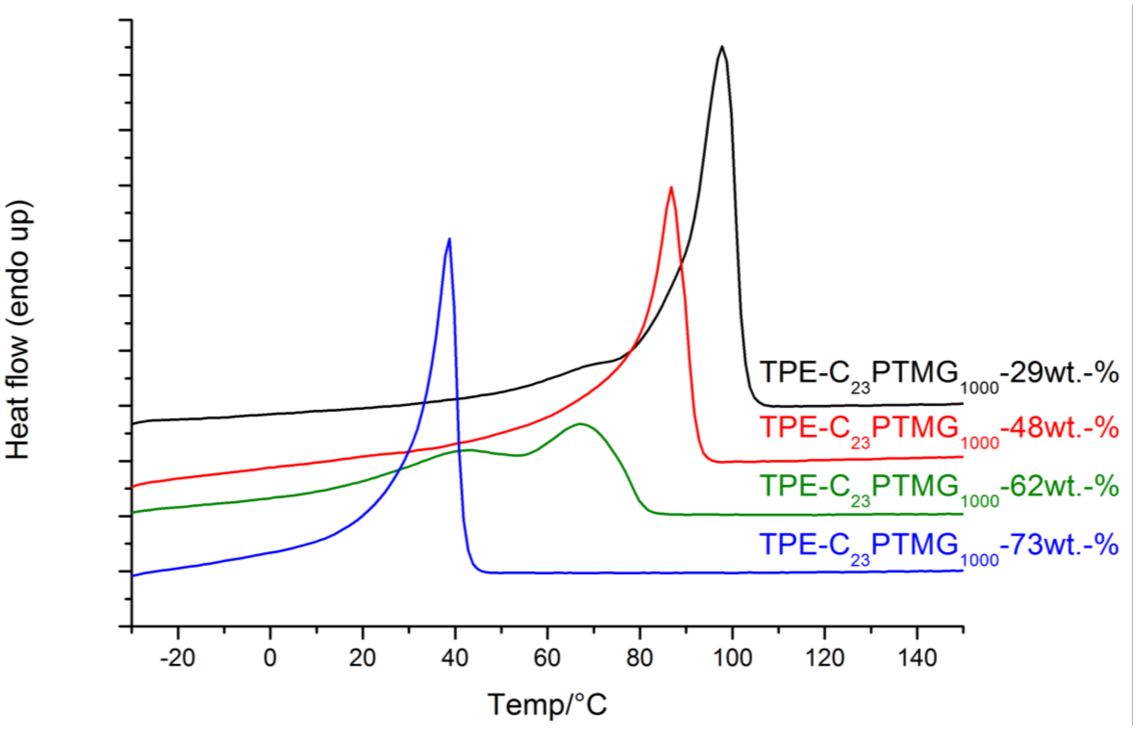


Figure 6.7: DSC thermograms (second heating) of polyester-polyether copolymers based on $PTMG_{1000}$.

Table 6.4: Polyester-polyether copolymers based on dodecanedioic acid and dodecanediol hard segments.

	sample	diacid	diol (1)	diol (2)	$M_{n,GPC}$[a] [g mol^{-1}]	T_m[b] [°C]	T_c[b] [°C]
1	TPE-$C_{12}PTMG_{1000}$-84wt.-%	4 (C_{12})	4 ($PTMG_{1000}$)		5.3×10^4	24	-4
2	TPE-$C_{12}PTMG_{1000}$-63wt.-%	4 (C_{12})	2 ($PTMG_{1000}$)	2 (C_{12})	6.2×10^4	52[c]	30[c]
3	TPE-$C_{12}PTMG_{2000}$-91wt.-%	4 (C_{12})	4 ($PTMG_{2000}$)		6.6×10^4	27	2
4	TPE-$C_{12}PTMG_{2000}$-77wt.-%	4 (C_{12})	2 ($PTMG_{2000}$)	2 (C_{12})	8.0×10^4	32[c]	5[c]
5[14]	TPE-$C_{12}PTMG_{2000}$-62wt.-%	7 (C_{12})	2 ($PTMG_{2000}$)	5 (C_{12})	5.5×10^4	17/66	1/45

[a] Determined by GPC in THF at 50 °C *vs.* polystyrene standards. [b] Determined by DSC with a heating/cooling rate of 10 K min^{-1}. [c] Broad melting and crystallization transitions are observed

6.4.3 Tensile testing

Dogbone-shaped sample bars for tensile testing (75 × 12.5 × 2 mm^3; ISO 527-2, type 5A) were prepared using a HAAKE Minijet II (Thermo Scientific) piston injection molder. The cylinder temperature and the mould temperature were set to 190 °C and 60 °C, respectively. All the samples were injected with an injection pressure and time of 500 bar and 3 s, and a post-pressure and time of 200 bar and 4 s, respectively.

After preconditioning the samples overnight tensile tests were performed on a Zwick Z005 and Zwick 1446 Retroline tC II instrument according to ISO 527 (crosshead speed 50 mm min^{-1}), with a determination of the Young modulus at a crosshead speed of 1 mm min^{-1}. The Zwick test Xpert software version 11.0 was used to collect and analyse the data. Young's modulus, stress at yielding, strain at yielding, tensile stress at break and elongation at break were obtained by averaging the data from several test specimens.

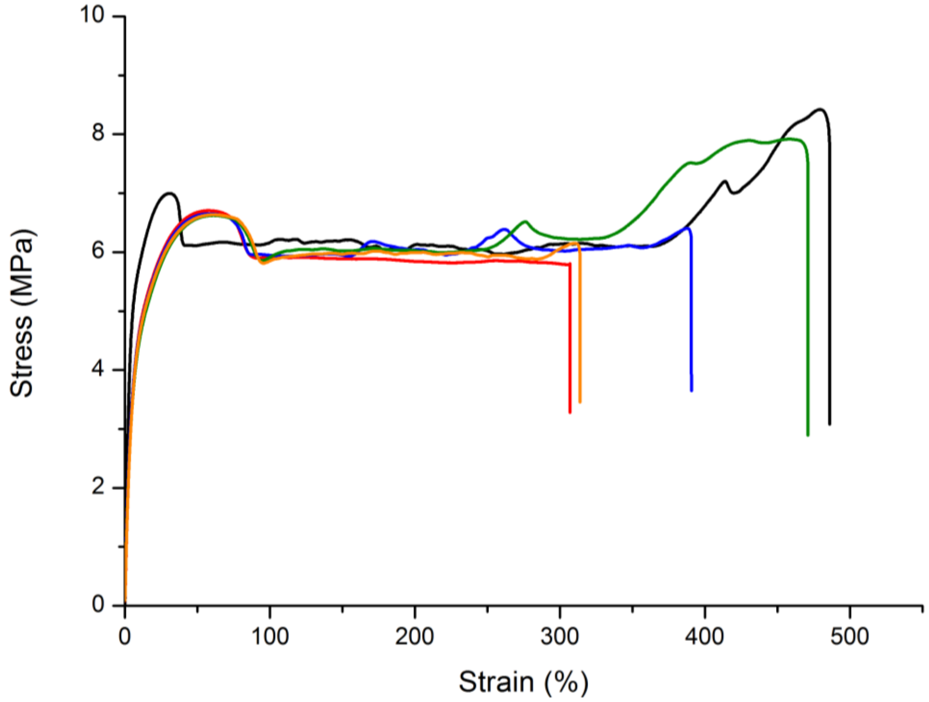


Figure 6.8: Stress-strain curves (constant drawing rate of 50 mm min^{-1}, room temperature) of TPE-$C_{23}PTMG_{1000}$-48wt.-%

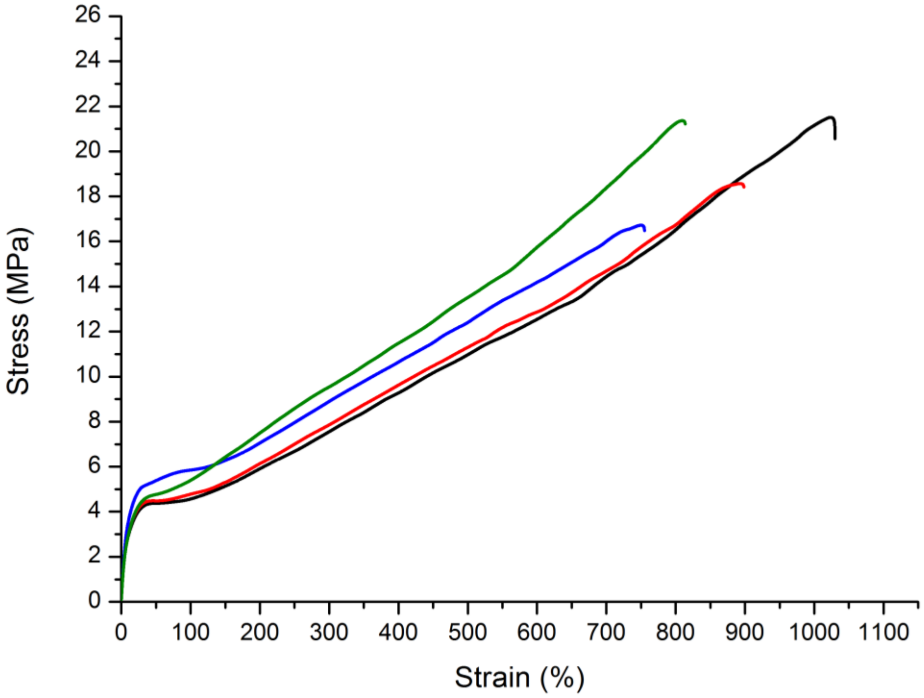


Figure 6.9: Stress-strain curves (constant drawing rate of 50 mm min^{-1}, room temperature) of TPE-$C_{23}PTMG_{2000}$-65wt.-%

6.4.4 Cyclic hysteresis tests

Cyclic hysteresis tests on dogbone-shaped sample bars (75 × 12.5 × 2 mm3; ISO 527-2, type 5A) of polyester-polyether copolymers were performed on a Zwick 1446 Retroline tC II instrument. The test specimens were repeatedly exposed to consecutive cycles of loading and unloading to a constant strain of 100 % with a constant crosshead speed of 50 mm min^{-1}. The recovery was measured by observing the residual strain after 10 cycles.

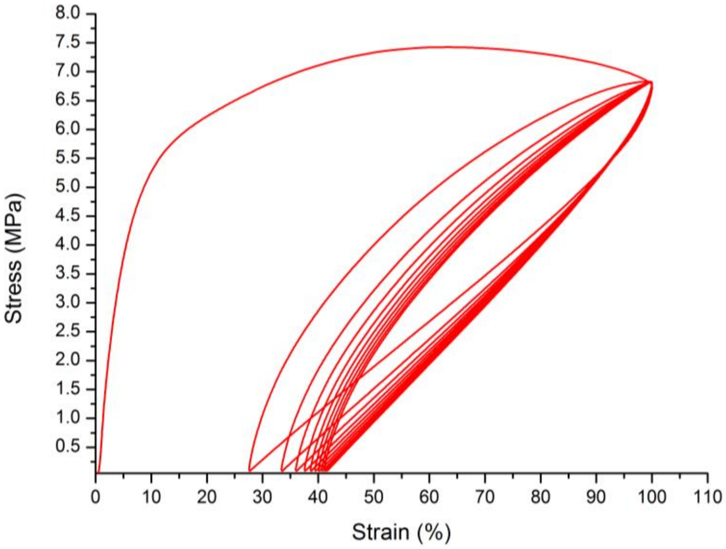


Figure 6.10: Stress-strain curves from cyclic tensile tests with a constant strain of 100 % for polyester-polyether copolymer TPE-$C_{23}PTMG_{1000}$-48wt.-% (10 cycles are displayed).

6.5 References

1. a) Ouhadi, T.; Abdou-Sabet, S.; Wussow, H.-G.; Ryan, L. M.; Plummer, L.; Baumann, F. E.; Lohmar, J.; Vermeire, H. F.; Malet, F. L. G., Thermoplastic Elastomers. in *Ullmann's Encyclopedia of Industrial Chemistry*, *Vol. 14* (Eds: Gerhartz, W.; Elver, B.), Wiley-VCH: Weinheim, **2000**, pp. 1-40. b) Holden, G.; Kricheldorf, H. R.; Quirk, R. P., *Thermoplastic Elastomers*. Hanser: Munich, **2004**.
2. a) Thermoplastic Elastomers. Holden, G.; Bishop, E. T.; Legge, N. R., *J. Polym. Sci. Part C: Polym. Symp.* **1969**, *26*, 37-57. b) Structure-Property Relationships for Styrene-Diene Thermoplastic Elastomers. Morton, M.; McGrath, J. E.; Juliano, P. C., *J. Polym. Sci. Part C: Polym. Symp.* **1969**, *26*, 99-115.
3. a) Renewable-Resource Thermoplastic Elastomers Based on Polylactide and Polymenthide. Wanamaker, C. L.; O'Leary, L. E.; Lynd, N. A.; Hillmyer, M. A.; Tolman, W. B. *Biomacromolecules* **2007**, *8*, 3634-3640. b) Polylactide-Poly(6-methyl-ε-caprolactone)-Polylactide Thermoplastic Elastomers. Martello, M. T.; Hillmyer, M. A. *Macromolecules* **2011**, *44*, 8537-8545. c) Thermoplastic Elastomers Derived from Menthide and Tulipalin. Shin, J.; Lee, Y.; Tolman, W. B.; Hillmyer, M. A., *Biomacromolecules* **2012**, *13*, 3833-3840. d) Sustainable Thermoplastic Elastomers Derived from Fatty Acids. Wang, S.; Vajjala Kesava, S.; Gomez, E. D.; Robertson, M. L. *Macromolecules* **2013**, *46*, 7202-7212.
4. a) The ATRP Synthesis of the Potential Thermoplastic Elastomer Poly(methyl methacrylate)-*b*-(lauryl methacrylate)-*b*-(methyl methacrylate). Chatterjee, D. P.; Mandal, B. M., *Macromol. Symp.* **2006**, *240*, 224-231. b) Synthesis, Morphology and Mechanical Properties of Linear Triblock Copolymers Based on Poly(α-methylene-γ-butyrolactone). Mosnáček, J.; Yoon, J. A.; Juhari, A.; Koynov, K.; Matyjaszewski, K., *Polymer* **2009**, 50, 2087-2094.
5. a) Catalyst Composition Comprising Shuttling Agent for Ethylene Multi-Block Copolymer Formation. Arriola, D. J.; Carnahan, E: M:; Cheung, Y. W.; Devore, D. D.; Graf, D. D.; Hustad, P. D.; Kuhlman, R. L.; Li Pi Shan, C.; Poon, B. C.; Roof, G. R.; Stevens, J. C.; Stirn, P. J.; Wenzel, T. T. (Dow Global Technologies), WO 2005/090427 (A2), **2005**. b) Catalytic Production of Olefin Block Copolymers via Chain Shuttling Polymerization. Arriola, D. J.; Carnahan, E. M.; Hustad, P. D.; Kuhlman, R. L.; Wenzel, T. T. *Science* **2006**, *312*, 714-719. c) Chain Shuttling Catalysis and Olefin Block Copolymers. Wenzel, T.; Arriola, D.; Carnahan, E.; Hustad, P.; Kuhlman, R. in *Topics in Organometallic Chemistry*, *Vol. 26* (Ed.: Guan, Z.), Springer Berlin/Heidelberg, **2009**, pp. 65-104.

6. Post-Metallocenes in the Industrial Production of Polyolefins. Baier, M. C.; Zuideveld, M. A.; Mecking, S. *Angew. Chem. Int. Ed.* **2014**, *53*, 9722-9744.
7. a) Thermoplastic Elastomers. Brown, M.; Witsiepe, W. K., *Rubber Age* **1972**, *104*, 35-42. b) Polyätherester-Block-Copolymere: Eine Gruppe Neuartiger Thermoplastischer Elastomere. Hoeschele, G. K.; Witsiepe, W. K., *Angew. Makromol. Chem.* **1973**, *29*, 267-289 c) Morphology of Segmented Polyester Thermoplastic Elastomers. Cella, R. J., J. *Polym. Sci: Polym. Symp.* **1973**, *42*, 727-740.
8. a) Lipid Biotechnology: Industrially Relevant Production Processes. Schörken, U.; Kempers, P. *Eur. J. Lipid Sci. Technol.* **2009**, *111*, 627-645. b) Biocatalytic and Fermentative Production of α,ω-Bifunctional Polymer Precursors. Schaffer, S.; Haas, T. *Org. Process Res. Dev.* **2014**, *18*, 752-766.
9. a) High Turnover Numbers with Ruthenium-Based Metathesis Catalysts. Dinger, M. B.; Mol, J. C. *Adv. Synth. Catal.* **2002**, *344*, 671-677. b) Metathesis of Unsaturated Fatty Acids: Synthesis of Long-Chain Unsaturated-α,ω-Dicarboxylic Acids. Ngo, H.; Jones, K.; Foglia, T. *J. Am. Oil Chem. Soc.* **2006**, *83*, 629-634.
10. a) Dicarboxylic Acid Esters from the Carbonylation of Unsaturated Esters under Mild Conditions. Jiménez-Rodriguez, C.; Eastham, G. R.; Cole-Hamilton, D. J. *Inorg. Chem. Commun.* **2005**, *8*, 878-881. b) Mechanistic Features of Isomerizing Alkoxycarbonylation of Methyl Oleate. Roesle, P.; Dürr, C. J.; Möller, H. M.; Cavallo, L.; Caporaso, L.; Mecking, S. *J. Am. Chem. Soc.* **2012**, *134*, 17696-17703.
11. a) Linear Semicrystalline Polyesters from Fatty Acids by Complete Feedstock Molecule Utilization. Quinzler, D.; Mecking, S. *Angew. Chem. Int. Ed.* **2010**, *49*, 4306-4308. b) Long-Chain Linear C_{19} and C_{23} Monomers and Polycondensates from Unsaturated Fatty Acid Esters. Stempfle, F.; Quinzler, D.; Heckler, I.; Mecking, S. *Macromolecules* **2011**, *44*, 4159-4166. c) Plant Oil-Based Long-Chain C_{26} Monomers and Their Polymers. Vilela, C.; Silvestre, A. J. D.; Meier, M. A. R. *Macromol. Chem. Phys.* **2012**, *213*, 2220-2227. d) Long-Chain Aliphatic Polyesters from Plant Oils for Injection Molding, Film Extrusion and Electrospinning. Stempfle, F.; Ritter, B. S.; Mülhaupt, R.; Mecking, S. *Green Chem.* **2014**, *16*, 2008-2014. e) Physical Properties and Hydrolytic Degradability of Polyethylene-Like Polyacetals and Polycarbonates. Ortmann, P.; Heckler, I.; Mecking, S. *Green Chem.* **2014**, *16*, 1816-1827.
12. Poly(tetramethylene ether glycol)/Poly(butylene terephthalate) Segmented Block Copolymers: Effects of Composition and Thermal Treatment on Thermal and Physical Properties. Choi, K. C.; Lee, E. K.; Choi, S. Y. *J. Ind. and Eng. Chem.* **2003**, *9*, 518-525.

13. NMR Investigations of In-Situ Stretched Block Copolymers of Poly(butylene terephthalate) and Poly(tetramethylene oxide). Schmidt, A.; Veeman, W. S.; Litvinov, V. M.; Gabriëlse, W., *Macromolecules* **1998**, *31*, 1652-1660.

14. Thermoplastic Polyester Elastomers Based on Long-Chain Crystallizable Aliphatic Hard Segments. Stempfle, F.; Schemmer, B.; Oechsle, A.-L.; Mecking, S. *Polym. Chem.* **2015**, *6*, 7133-7137.

15. Press release by BASF of March 5, 2015.

7 Synthetic polyester from algae oil

7.1 Introduction

A potential drawback of biomass from land plants, including the seed oils employed in the previous chapters, are the consumption of land and irrigation water, a competition with food production, inefficient yields per time and area and the associated logistics of harvesting and collection.[1]

Before this background, algae oils are currently receiving much awareness. Microalgae can be cultivated in brackish or seawater on non-arable land that is unapt for food production. Furthermore, no costly nutrients like glucose or peptones are required necessarily.[2] Rather, sunlight and CO_2 may serve as an energy source and raw material, respectively. The relatively high division rates of individual algal strains may result in a duplication of the biomass within 24 hours.[3] At the same time, the amount of fatty acids in microalgae can be substantial with around 20-50 % of the dry weight.[3,4]

While these advantages of algae oils are often and increasingly highlighted,[5,6,7] the application of algae oils so far is mostly restricted to the extraction of the naturally occurring ingredients and their utilization as biofuels, pigments, vitamins or for human and animal nutrition. A prominent example are polyunsaturated ω-3 fatty acids used as food additives. On the other hand, efforts to use algae oils industrially comprise deoxygenation, pyrolysis or even gasification to C_1 building blocks and their subsequent Fischer-Tropsch conversion to higher alkanes. All these studies aim at using algae oil to generate hydrocarbons that ideally cannot be differentiated from the corresponding fractions, like jet fuel, based on crude oil.[8,9] However, the production of algae is associated with an energy input which currently still has a significant impact on the overall balance of fuel generation. This supports the general perception that generation of more valuable products than fuels for combustion is worthwhile. Interestingly, algae not only produce large amount of lipids, they are also a unique resource for 'unusual' classes of lipids and fatty acids differing from those available from higher animals and plant organisms.[10] This opens up unique opportunities for the production of chemicals from these oils, which may have a broader variety of structures and which can also be tailored specifically for sophisticated applications. As an example of the idea of translating the unique feedstock structure of algae oil into otherwise inaccessible structures, in this chapter the feasibility of the synthesis of long-chain α,ω-difunctional compounds and of the corresponding polyesters was studied (**Figure 7.1**).

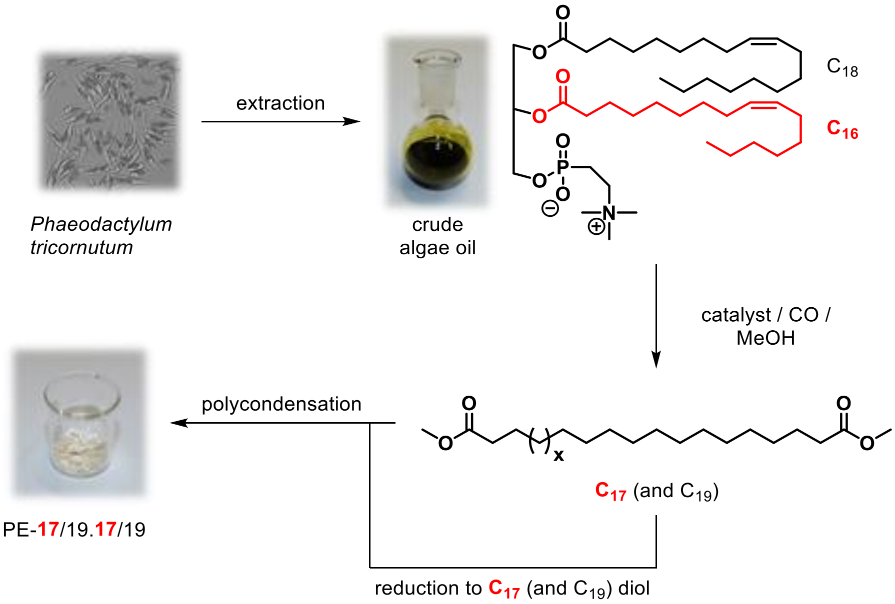


Figure 7.1: Exemplary approach to yield mixed, linear long-chain aliphatic polyester from algae.

7.2 Results and discussion

The diatom *Phaeodactylum tricornutum* was chosen as a source for lipids, as published data suggested this strain to be very effective in the production of the desired unsaturated fatty acids.[11,12] This species belongs to the group of diatoms, ubiquitously present in aquatic and unicellular microalgae, which are major players in the global carbon cycle with an estimated share of up to 20 % of total global carbon fixation.[13,14] Furthermore the genomic information of this algae is available[15] and genetic manipulation is feasible.[16]

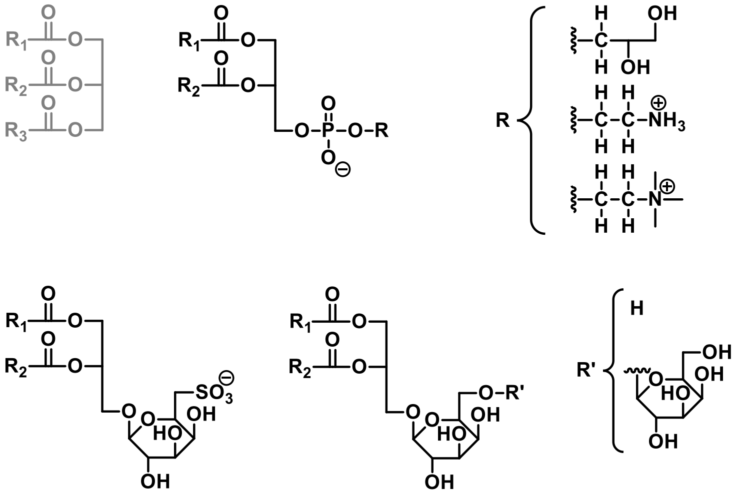


Figure 7.2: Fatty acids (R$_1$-R$_3$) as they appear in plants (grey, top left) and algae (black).

In contrast to traditional plant oils,[17,18,19] algae do not contain fatty acids primarily in the form of triacylglycerides, but rather as diacylglycerides substituted with polar substituents such as galactosyl or phosphate groups on the third hydroxyl moiety of glycerol (**Figure 7.2**).[20] This feature is important, as direct extraction of fatty acids with hydrocarbon solvents is thus not possible. Note, that also triacylglycerides can be present, especially when the algae are in the stationary growth phase for a longer period.

7.2.1 Growth and extraction of algae

Phaeodactylum tricornutum was grown in 10 L flasks in f/2-medium with half concentrated sea water compounds at a light intensity of 35 μmol s^{-1} m^{-2} in a day/night rhythm of 16/8 hours at 20 °C. The algae was cultivated for 3-4 weeks, being in the stationary phase for at least 3 weeks. Depending on the algae batch, the cell counts were around 10^{7} mL^{-1}. After centrifugation, 30-45 g of algae (wet weight) were obtained per 30 L of growth medium. Freeze drying of 45 g of the algae yielded 13 g of dry algae (for detailed procedures see Experimental section).

In the late stationary phase *Phaeodactylum tricornutum* starts accumulating visible lipid droplets (**Figure 7.3**; left). In order to destroy the cellular membrane and to extract the fatty acids, different techniques were tested. Direct Soxhlet extraction using heptane as a solvent resulted in 0.1 g of extracted algae oil, which is far below literature data suggesting that around 2-3 g of algae oil should be obtained from such a 30 L culture.[11] This low yield is likely due to the fatty acids being present as diacylglycerides substituted with polar substituents (*vide supra*) and thus being hardly soluble in apolar solvents such as heptane. Thus, acidic hydrolysis of the ester functionalities was applied. For this purpose concentrated hydrochloric acid was added to the algae broth and the resulting dark-green suspension was heated to reflux for 12 hours. After neutralization with $NaHCO_3$ followed by subsequent centrifugation, the solid residues were Soxhlet-extracted with heptane and the supernatant was extracted with methylene chloride yielding in total 1.3 g of algae oil. However, as further evidenced by light microscopy, acidic hydrolysis as well as mechanical disintegration was needed to release the lipid droplets from the cells (**Figure 7.3**; right).

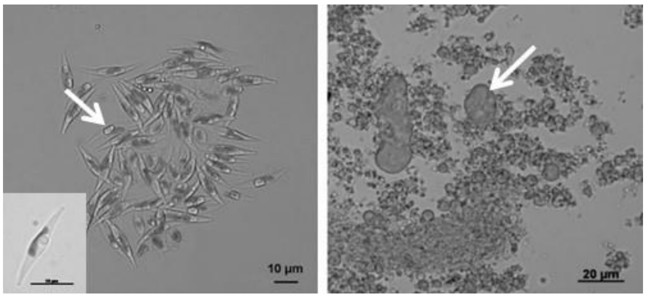


Figure 7.3: Light microscopical images of *Phaeodactylum tricornutum* before (left) and after (right) treatment with ultrasound and acidic hydrolysis. Insert in left image shows a single cell, the dark area being a chloroplast. The arrows indicate lipid droplets in the intact cells (left) and released lipids after breaking the cells (right).

Lipid extraction after acidic hydrolysis and treatment with ultrasound yielded 2.6 g of dark green algae oil. Appling this procedure to algae cultures with prolonged cultivation times (stationary phase about 6 weeks) up to 5.8 g of algae oil can be obtained. These results compare favorably with optimized yields reported from established methods for lipid extraction.[21,22]

7.2.2 Identification and monomer generation from fatty acids in algae oil

Fatty acids in the extracted algae oil were identified via gas chromatography (GC) by comparison of retention times and enrichment with genuine samples of the respective fatty acids (**Figure 7.4**). 48.2 % of monounsaturated fatty acids (37.0 % palmitoleic acid (16:1)[23] and 11.2 % oleic acid (18:1)), 16.2 % of the multiple unsaturated fatty acid eicosapentaenoic acid (20:5) and 35.0 % of saturated fatty acids (23.4 % palmitic acid (16:0) and 11.6 % myristic acid (14:0)) were identified. However, as already suggested by its green color and evidenced by gas chromatography not only fatty acids are present in the algae oil. Possible ingredients, both ubiquitously present in algae, may be carotenoids or chlorophylls.

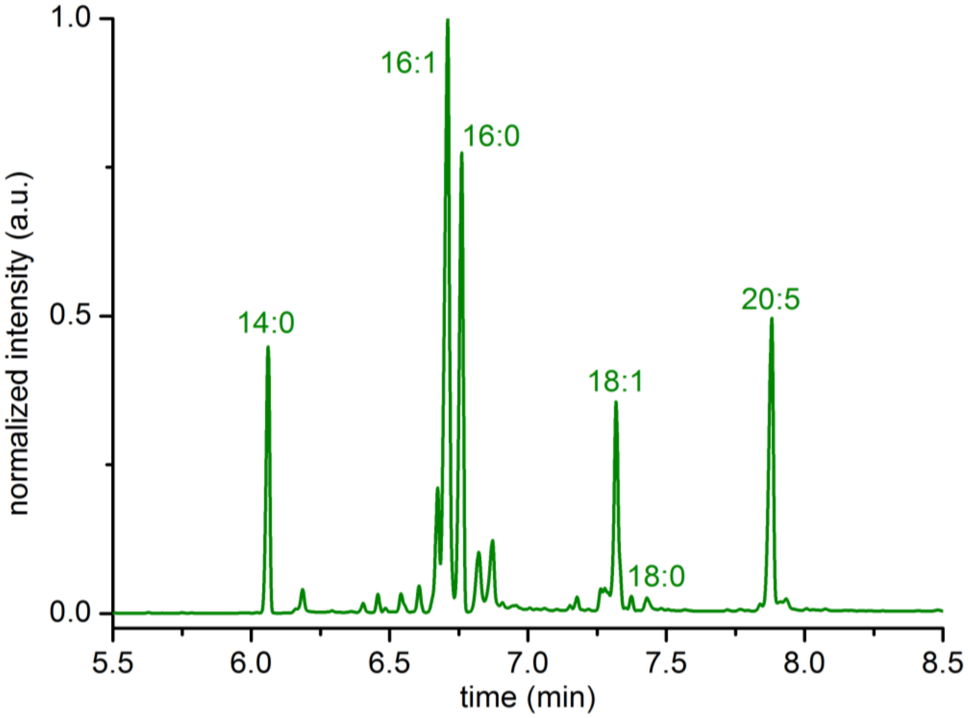


Figure 7.4: GC trace of crude algae oil extracted from *Phaeodactylum tricornutum* (after transesterification to the methyl esters for analysis).

A synthesis of polyesters via polycondensation requires further conversion to difunctional molecules as monomers. This requires catalysts compatible with the various components of the crude algae oil. For example, the phosphate moieties may block coordination sites detrimentally, particularly for electrophilic cationic active species. Tetraalkyl ammonium salts may alkylate phosphine ligands. The activity of (neutral) ruthenium alkylidene metathesis catalysts was reported to be decreased tremendously by phosphates, for example.[24]

Before this background, the extracted algae oil (5.8 g) was exposed to 20 bar CO pressure at 90 °C in methanol as a reagent and solvent in a pressure reactor in the presence of [(dtbpx)Pd(OTf)](OTf) (970 µmol; dtbpx = 1,2-bis((di-*tert*-butylphosphino)methyl)benzene) as an established catalyst precursor for isomerizing methoxycarbonylation.[25,26,27] GC analysis of the crude reaction mixture (**Figure 7.5**, top trace) clearly evidences, that the monounsaturated fatty acids (16:1 and 18:1) are converted virtually completely to the desired linear 1,17- and 1,19-diester, respectively. These diesters were assigned unambiguously by enrichment with genuine samples prepared independently via methoxycarbonylation of pentadeca-1,14-diene and methyl oleate, respectively (cf. **Chapter 7.2.3** and Experimental section). The signal of eicosapentaenoic acid also disappeared during the isomerizing methoxycarbonylation of the algae oil. Apparently, eicosapentaenoic acid was not transformed to the 1,21-diester as evidenced by hydrogenation of the reaction mixture and enrichment with a genuine sample (for preparation of this 1,21-diester see **Chapter 7.2.3** and Experimental section). Possible reaction pathways may be multiple methoxycarbonylation or hydromethoxylation.[28] Recrystallization from methanol and heptane yielded 2.1 g of a mixture of 82 % 1,17- and 18 % 1,19-diester in polycondensation grade purity (> 99 %, **Figure 7.5**, bottom trace). A part of this mixture was reduced to the respective diols using $LiAlH_4$. After recrystallization from chloroform a mixture of 85 % 1,17- and 15 % 1,19-diol was obtained in polycondensation grade purity (> 99 %). The ratio between the diols with different chain length was slightly different from the ratio of its respective diesters, presumably due to different solubility of the diols in the recrystallization. However, this is not a problem for the following polycondensation reaction (cf. **Chapter 7.2.4**).

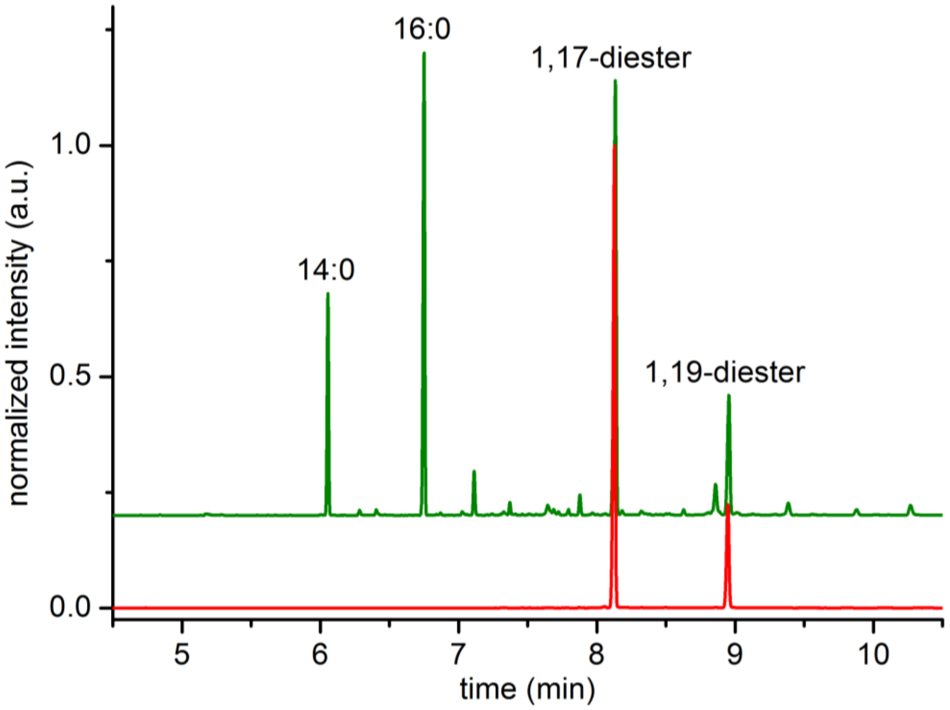


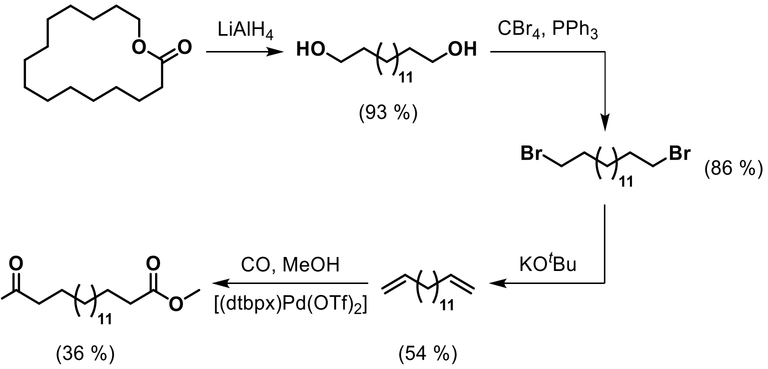
Figure 7.5: GC trace of the crude reaction mixture obtained from the isomerizing methoxycarbonylation of algae oil (top, green), and after recrystallization from methanol and heptane (bottom, red).

7.2.3 Synthesis of genuine samples of 1,17-; 1,21- and 1,25-diester and corresponding model Polyesters-X.X (X = 17, 21 and 25)

In order to unambiguously identify the possible reaction products obtained in the isomerizing methoxycarbonylation of monounsaturated fatty acids from crude algae oil, linear long-chain diesters, namely dimethyl-1,17-heptadecanedioate (1,17-diester), dimethyl-1,21-henicosanedioate (1,21-diester) and dimethyl-1,25-pentacosanedioate (1,25-diester) were prepared. For the synthesis of these model compounds different multistep syntheses using alkoxycarbonylation of α,ω-dienes as the key step are applied. After reduction of the aforementioned diesters these novel linear-long chain components were furthermore utilized as starting materials for the preparation of neat model polyesters-X.X (X = 17, 21 and 25).

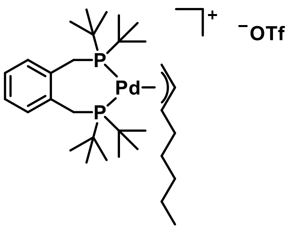
Synthesis of dimethyl-1,17-heptadecanedioate

Reduction of oxacyclohexadecan-2-one (a component of *Angelica archangelica L.* root oil)[29] by means of $LiAlH_4$ yielded pentadecane-1,15-diol.[30] Conversion of the resulting diol into the α,ω-dibromide, followed by elimination of HBr, gives access to pentadeca-1,14-diene. The desired linear long-chain diester, namely dimethyl-1,17-heptadecanedioate, was generated by subsequent alkoxycarbonylation of the α,ω-diene in an overall yield of 16 % (**Scheme 7.1**).



Scheme 7.1: Synthesis of dimethyl-1,17-heptadecanedioate.

In the last reaction step prolonged reaction times (up to 7 days) were applied due to slower reaction rates reported for the isomerizing alkoxycarbonylation of multiple unsaturated compounds. From literature it is known, that such compounds can form thermodynamic stable, monosubstituted/terminal Pd-allyl species, upon reaction with the catalytically active Pd-hydride complexes. Octa-1,7-diene for example in presence of the deuteride species $[(dtbpx)Pd(D)(CD_3OD)]^+(OTf)^-$ is quantitatively converted into $[(dtbpx)Pd(\eta^3\text{-}C_3H_4)\{(CH_2)_4CH_3\}]^+(OTf)^-$ (**Scheme 7.2**).[31]

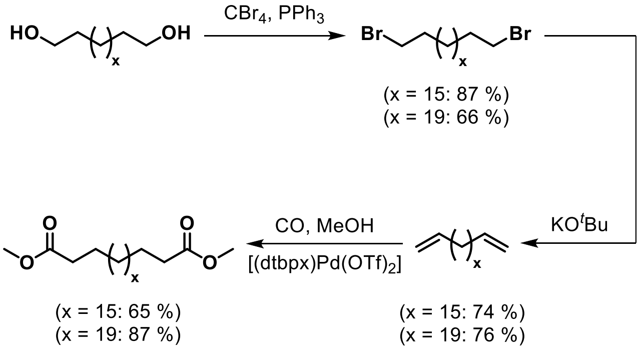


Scheme 7.2: Monosubstituted/terminal Pd-allyl species generated from [(dtbpx)Pd(D)(CD$_3$OD)]$^+$(OTf)$^-$ and octa-1,7-diene.

Nevertheless the lower yield observed here for the alkoxycarbonylation of pentadeca-1,14-diene can be also ascribed to product loss during recrystallization due to the higher solubility of the C$_{17}$-component compared to its longer chain analogues.

Synthesis of dimethyl-1,21-henicosanedioate and dimethyl-1,25-pentacosanedioate

Nonadecane-1,19-diol (obtained by isomerizing alkoxycarbonylation of methyl oleate and subsequent reduction of the linear long-chain diester to the corresponding diol) was transformed into dimethyl-1,21-henicosanedioate with an overall yield of 42 % by bromination, elimination of HBr and subsequent alkoxycarbonylation of the resulting α,ω-diene. Applying this reaction sequence to tricosane-1,23-diol, the even longer chain dimethyl-1,25-pentacosanedioate can be generated with an overall yield of 44 % (**Scheme 7.3**).



Scheme 7.3: Synthesis of dimethyl-1,21-henicosanedioate (x=15) and dimethyl-1,25-pentacosanedioate (x=19).

The corresponding long-chain α,ω-diols were generated by reduction of the aforementioned diesters, stoichiometrically with LiAlH$_4$ or by catalytic hydrogenation with Saudan's[32] ruthenium catalyst.

Synthesis of PE-17.17, PE-21.21 and PE-25.25

Polycondensation of these difunctional A$_2$+B$_2$ monomers catalyzed by titanium alkoxides afforded the corresponding long-chain aliphatic polyesters, namely poly[1,17-heptadecanediyl-1,17-heptadecanedioate] (**PE-17.17**), poly[1,21-henicosanediyl-1,21-henicosanedioate] (**PE-21.21**) and poly[1,25-pentacosanediyl-1,25-pentacosanedioate] (**PE-25.25**).

Table 7.1: Molecular weights and thermal properties of long-chain aliphatic polyesters.

entry	T_m[a] [°C]	T_c[a] [°C]	$M_{n,NMR}$[b] [g mol^{-1}]	$M_{n,GPC}$[c] [g mol^{-1}]	M_w/M_n[c]
PE-17.17	99	76	2.6×10^4	2.5×10^4	4.0
PE-21.21	104	80	3.6×10^4	3.9×10^4	3.7
PE-25.25	108	86	2.2×10^4	2.3×10^4	3.4

[a] Determined by DSC with a heating/cooling rate of 10 K min^{-1}.
[b] Determined by end-group analysis from ^{1}H-NMR spectroscopy.
[c] Determined by GPC at 160 °C in trichlorobenzene *vs.* polyethylene standards.

End-group analysis by ^{1}H-NMR spectroscopy, as well as high temperature GPC measurements relative to polyethylene standards, revealed number-average molecular weights on the order of several 10^4 g mol^{-1} (**Table 7.1**). As determined by DSC **PE-17.17** exhibits a melting point of T_m = 99 °C (T_c = 76 °C, ΔH_m = 141 J g^{-1}). For the even longer chain aliphatic polyester **PE-21.21** a melting point of T_m = 104 °C (T_c = 80 °C, ΔH_m = 159 J g^{-1}) was found, whereas thermal analysis of **PE-25.25** reveals a further increase of the melting temperature to T_m = 108 °C (T_c = 86 °C, ΔH_m = 157 J g^{-1}).

7.2.4 Preparation of mixed linear long-chain aliphatic polyester from algae oil

In order to achieve any substantial molecular weight by means of classical step-growth polycondensation reactions a very accurate control of the stoichiometric ratio of functional groups is necessary.[33] To this end, the appropriate amount of the diol and the diester components, generated from the algae oil, were calculated from the peak area percentage obtained from the GC analyses (cf. Experimental section). Polycondensation catalyzed by titanium alkoxides afforded a mixed linear long-chain polyester **PE-17/19.17/19**[34] with a number average molecular weight of $M_n = 4.0 \times 10^4$ g mol^{-1} as determined by both ^{1}H NMR spectroscopic analysis of the end groups and high temperature GPC. The material prepared showed a melting point of T_m = 99 °C (T_c = 75 °C, ΔH_m = 136 J g^{-1}, **Figure 7.9**).

Other than known long-chain polyesters, the material prepared here contains a mixture of repeat units of different carbon number (C_{17} and C_{19}). Such a less regular spacing of the ester groups could hinder the formation of sheets of ester groups and result in reduced order and melting points.[35-38] However, no such adverse effect was observed and the melting points are in line with neat model polyesters-X.X (**Figure 7.6**) prepared from the genuine samples for gas chromatographic identification (X = 17: T_m = 99 °C; X = 21: T_m = 104 °C and X = 25: T_m = 108 °C, cf. Experimental section for details) and reported data for other polyesters-X.X with odd numbers of carbon atoms in the repeat units (X = 19: T_m = 103 °C[26] and X = 23: T_m = 108 °C[39]).

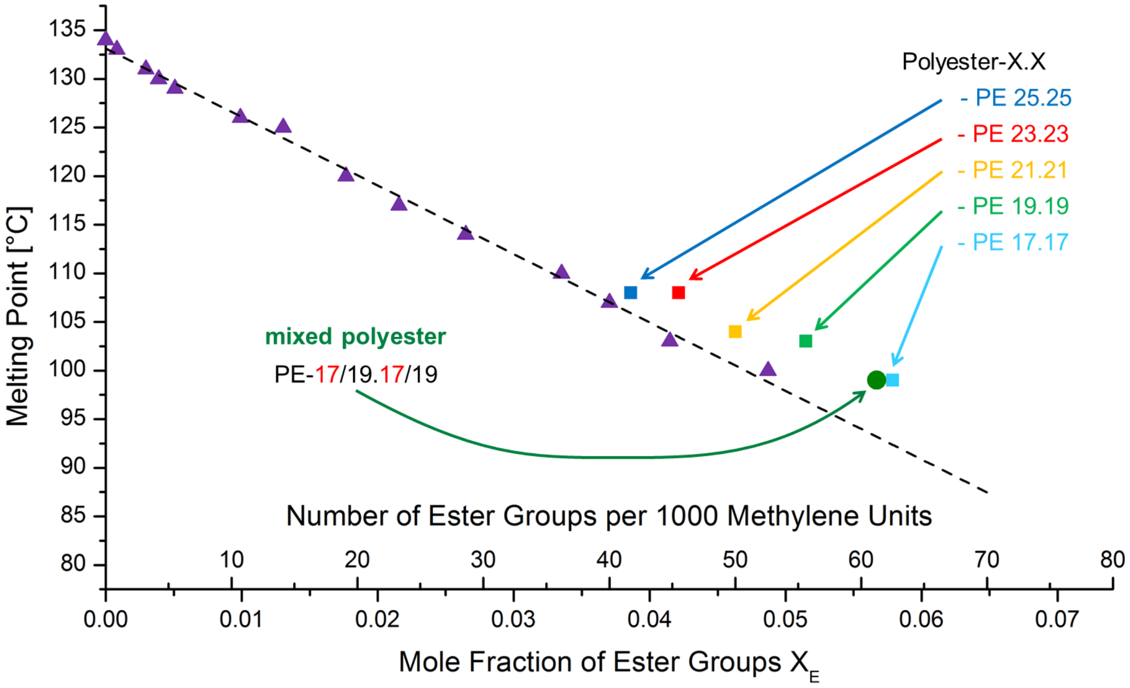
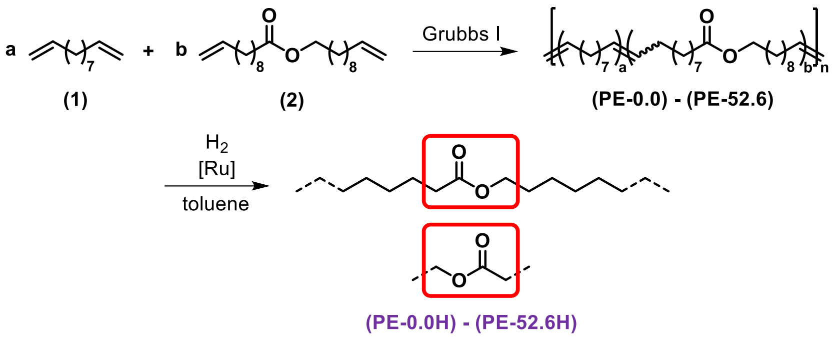


Figure 7.6: Peak melting points (T_m) of random long-spaced polyesters from ADMET copolymerization[38] (▲) and symmetrical regularly spaced long-chain A_2+B_2 type polyesters (■), as well as mixed polyester from algae oil (●), *vs.* number of ester groups per 1000 CH_2 and mole fraction X_E.

Hereby, with increasing amount of long, crystallizable methylene segments within the diacid- and diol-component as well, melting temperatures converge towards linear polyethylene. In this way aliphatic polyesters with melting points exceeding 100 °C suitable for thermoplastic processing can be obtained starting from readily available plant oils as well as algae oil. This is of particular importance as, apart from the very short-chain aliphatic polyesters like poly(lactide acid) (PLA) or poly(butylene succinate) (PBS), aliphatic polyesters accessible from current diacid and diol monomers, based on petrochemical as well as renewable feedstocks, suffer from their low melting points.[40]

By contrast to long-spaced aliphatic model polyesters, synthesized by random acyclic diene metathesis (ADMET) copolymerization of undeca-1,10-diene (**1**) and undec-10-en-1-yl undec-10-enoate (**2**) followed by exhaustive hydrogenation (**Scheme 7.4**),[38] the regular spaced long-chain A_2+B_2 type polyesters generated from diesters and diols with identical numbers of carbon atoms, as well as the mixed polyester **PE-17/19.17/19** exhibit slightly higher melting points than the ADMET-derived polyesters containing a comparable number of, however, randomly distributed ester groups (cf. **Figure 7.6**).



Scheme 7.4: Synthesis of long-spaced aliphatic model polyester via ADMET copolymerization of undeca-1,10-diene and undec-10-en-1-yl undec-10-enoate and subsequent exhaustive post-polymerization hydrogenation.[38]

This effect can be related to the ability of polyesters to form layers of ester groups by noncovalent interactions between the chain segments in the polymer lattice, when the polyesters crystallize in a planar zigzag chain conformation.[36,41] Due to the homogeneous spacing in the case of regularly spaced A_2+B_2 type polyesters, the details of one ester layer can be reproduced in the neighboring ester layers in the same crystal by the orientation of the ester dipoles.[36] This effect appears to diminish for longer regularly spaced polyesters (cf. **Figure 7.6**).

Although having repeat units of different carbon number (C_{17} and C_{19}), the melting temperature of mixed polyester **PE-17/19.17/19**, is still in line with regularly spaced A_2+B_2 type polyesters generated from diesters and diols with identical numbers of carbon atoms. This observation might be attributed to the relatively high portion of the C_{17}-components (of about 85 %) as well as the absence of irregular incorporation of ester groups found in the polymers generated via ADMET copolymerization, where the ester groups are randomly distributed over the polymer chain and in addition also exhibit a random orientation of the ester groups in the chain ($-OC(=O)(CH_2)_xC(=O)O-$ *vs.* $-O(CH_2)_yC(=O)-/-C(=O)(CH_2)_zO-$).

7.3 Conclusion

Current efforts to technically use microalgae focus on the generation of fuels with a molecular structure identical to crude oil based products. Here a different approach for the utilization of algae by translating the unique molecular structures of algae oil fatty acids into higher value chemical intermediates and materials is suggested. This requires appropriate chemical conversions and catalysts compatible with algae oil. In an exemplary approach (**Figure 7.1**) polyesters were synthesized from crude lipids of the diatom *Phaeodactylum tricornutum*. First findings support the feasibility of the generation of functional chemical intermediates by modern catalytic methods from algae oil, as exemplified by the preparation of dimethyl-1,17-heptadecanedioate and heptadecane-1,17-diol. These molecules are based on a C_{16} building block (palmitoleic acid) which is a major component of algae oils but not of traditional plant oils. α,ω-Difunctional compounds can be obtained in high purity by isomerizing alkoxycarbonylation, even enabling step-growth polycondensation to high molecular weight polyester. This novel polyester possesses an advantageously high melting point of T_m = 99 °C as a result of the crystallizable linear segments originating from the algae oil lipids.

Notably, the transition metal catalyzed methoxycarbonylation is possible on the crude algae extract. Neither the five-fold unsaturated eicosapentaenoic acid nor other non-fatty acid components of the algae (amongst others phosphocholines, cf. **Figure 7.2**) shut down catalysis. While an optimization of the work-up procedures for larger scale synthesis was not a focus of this work, it can be noted that already at this stage no complicated chromatographic workup of the products of catalysis was necessary but rather a recrystallization, which can be readily scaled, was sufficient.

7.4 Experimental section

7.4.1 Materials and general considerations

Unless stated otherwise, all manipulations were carried out under an inert gas atmosphere using standard Schlenk or glovebox techniques. Methanol was distilled from magnesium turnings and iodine prior to use. THF and toluene were distilled from sodium under inert conditions. All other solvents were used in technical grade as received. Carbon monoxide (3.7) was supplied by Air Liquide. Dimethyl-1,19-nonadecanedioate, nonadecane-1,19-diol, and [(dtbpx)Pd(OTf)](OTf) were prepared according to a literature procedure (also cf. **Chapter 5.4.2**).[42] Titanium(IV) butoxide (≥ 97 %), $LiAlH_4$, $MgSO_4$, $NaHCO_3$, oxacyclohexadecan-2-one, NaOH and CBr_4 were purchased from Sigma-Aldrich. PPh_3 and KOtBu were purchased from Acros. All chemicals were used as received. Deuterated solvents, supplied by Eurisotop, were stored over 4 Å molecular sieves under argon or nitrogen.

NMR spectra were recorded on a Varian Inova 400, a Bruker Avance 400 and on a Bruker Avance DRX 600 spectrometer. ^1H and ^{13}C chemical shifts were referenced to the solvent signals. High-temperature NMR measurements of polymers were performed in 1,1,2,2-tetrachloroethane-*d2* at 130 °C. Acquired data was processed and analysed using MestReNova software.

Elemental analyses were performed up to 950 °C on a Elementar Vario EL instrument.

Gas chromatography was carried out on a PerkinElmer (PE) Clarus 500 instrument with autosampler and FID detection on a PerkinElmer Elite-5 (5 % Diphenyl- 95 % Dimethylpolysiloxane) Series Capillary Columns (Length: 30 m, Inner Diameter: 0.25 mm, Film Thickness: 0.25 mm), using Helium as carrier gas at a flow rate of 1.5 mL min^{-1}. The injector temperature was 300 °C. After injection the oven was kept isothermal at 90 °C for 1 min, heated with 30 K min^{-1} to 280 °C, and kept isothermal at 280 °C for 8 min (for the 1,25-diester the injector temperature was 270 °C and the oven was kept isothermal at 100 °C for 1 min, heated with 15 K min^{-1} to 300 °C, and kept isothermal at 300 °C for 5 min).

DSC was measured on a Netzsch DSC 204 F1 with a heating and cooling rate of 10 K min^{-1} in a temperature range of -50 to 160 °C. All data are referred to the second heating cycle.

High temperature GPC measurements were carried out in 1,2,4-trichlorobenzene at 160 °C at a flow rate of 1 mL min^{-1} on a Polymer Laboratories 220 instrument equipped with Olexis columns with differential refractive index, viscosity, and light-scattering (15° and 90°) detectors. Data reported were determined directly against polyethylene standards.

Algae was centrifuged on a Sorvall RC 6 centrifuge with a Sorvall SLA 3000 rotor at 4900 turns min^{-1} for 10 minutes at 4 °C. Light microscope images were recorded on an Olympus BX 51 equipped with a Zeiss AxioCam MRm. Cell counts were determined using the coulter counter Multisizer 3 from Beckmann Coulter.

7.4.2 Cultivation of algae

Phaeodactylum tricornutum UTEX 646 was obtained from the Culture Collection of Algae at the University of Texas in Austin and grown in 10 L flasks in a modified f/2-medium[43,44] (pH = 7) with artificial half concentrated sea salts (16.6 g L^{-1}, tropic marine) and 0.09 µM $MnCl_2$ at a light intensity of 35 µmol s^{-1} m^{-2} in a day/night rhythm of 16/8 hours at 20 °C. Ambient air was bubbled through the flasks. The algae was cultivated for 7-8 weeks, being in the stationary phase for at least six weeks.

7.4.3 Extraction of fatty acids from algae

Extraction of fatty acids from algae - method I:

The cell count was $9.35 \cdot 10^6$ mL^{-1}. 30 L of algae culture were centrifuged yielding 41.9 g of wet algae. The wet solid was soxhlet extracted with 300 mL of heptane for 4 hours. Heptane was removed under reduced pressure to yield 100 mg of green algae oil.

To increase the yield, the solid was dispersed in water and treated according to method III, to yield another 600 mg of algae oil.

Extraction of fatty acids from algae - method II:

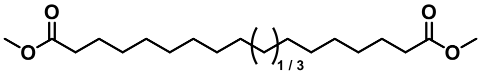
The cell count was $8.63 \cdot 10^6$ mL^{-1}. 30 L of algae culture were centrifuged yielding 30.4 g of wet algae. The wet algae was transferred into a flask and conc. HCl was added until pH = 1. After heating to reflux overnight, saturated $NaHCO_3$ was added until pH = 6-7, and the resulting suspension was centrifuged. Solids were separated, dried and soxhlet extracted with 300 mL of heptane overnight. The water phase was extracted with methylene chloride (4 x 250 mL). The combined organic layers were dried over $MgSO_4$. After removing the solvent, 1.32 g of green algae oil were obtained.

Extraction of fatty acids from algae - method III:

The cell count was $10.76 \cdot 10^6$ mL^{-1}. 30 L of algae culture were centrifuged yielding 45.3 g of wet algae. After freeze drying, 12.8 g of dry algae were obtained. The solid was dispersed in 200 mL of water and ultrasonicated for 30 minutes. Conc. HCl was then added until pH = 1. After heating to reflux overnight, saturated $NaHCO_3$ was added until pH = 6-7, and the resulting suspension was centrifuged. Solids were separated, dried and soxhlet extracted with 300 mL of heptane for 5 h. The water phase was extracted with methylene chloride (4 x 250 mL). The combined organic layers were dried over $MgSO_4$. After removing the solvent, 2.63 g of green algae oil were obtained. Appling this extraction method to algae cultures with prolonged cultivation times (stationary phase about 6 weeks) up to 5.83 g of algae oil can be obtained.

7.4.4 Isomerizing methoxycarbonylation of algae oil

According to the general methoxycarbonylation procedure, algae oil (5.8 g) and [(dtbpx)Pd(OTf)](OTf) (776.5 mg, 0.97 mmol) were dissolved in 100 mL of methanol. The resulting solution was transferred into the pressure reactor, which was pressurized with 20 bar CO and heated to 90 °C for 7 days while stirring the reaction mixture. The resulting suspension was diluted with methylene chloride and filtered to remove solids. After removing the solvents under reduced pressure, the crude product was recrystallized from methanol and heptane to yield a mixture of the desired 1,17- (82 %) and 1,19- (18 %) diester products in polycondensation grade purity (2.1 g, 6.3 mmol, molecular weight calculated from GC data).



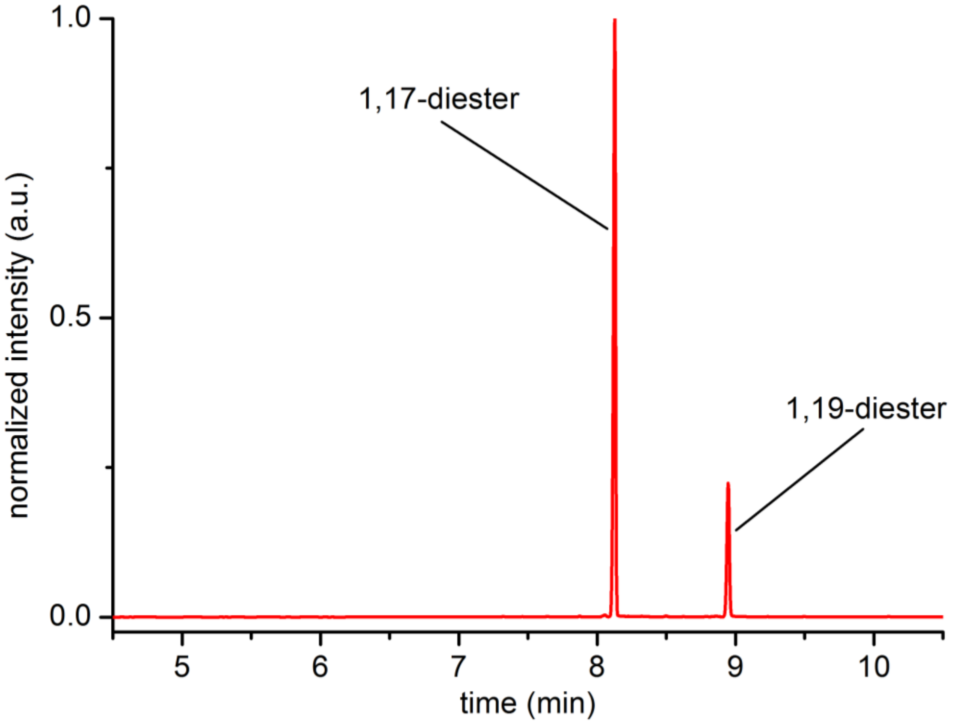
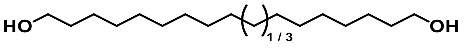


Figure 7.7: GC trace of mixed 1,17- and 1,19-diester after recrystallization from methanol and heptane.

7.4.5 Reduction of diesters from the isomerizing methoxycarbonylation of algae oil

A part of the diester mixture obtained in the isomerizing methoxycarbonylation (600 mg, 1.8 mmol) was dissolved in 7 mL of THF and added dropwise to a cooled suspension (0 °C) of $LiAlH_4$ (178 mg, 4.7 mmol) in 10 mL of THF. After complete addition, the suspension was refluxed for 1 h and stirred for 3 days at room temperature. Then, 2 mL of water and 0.5 mL of a

2 M NaOH solution were added and the resulting precipitate was filtered off. Volatiles were removed under reduced pressure and the resulting solid was recrystallized from $CHCl_3$ yielding 358.3 mg of the desired 1,17- (85 %) and 1,19- (15 %) diol products in polycondensation grade purity (1.3 mmol, 72 %, molecular weight calculated from GC data).



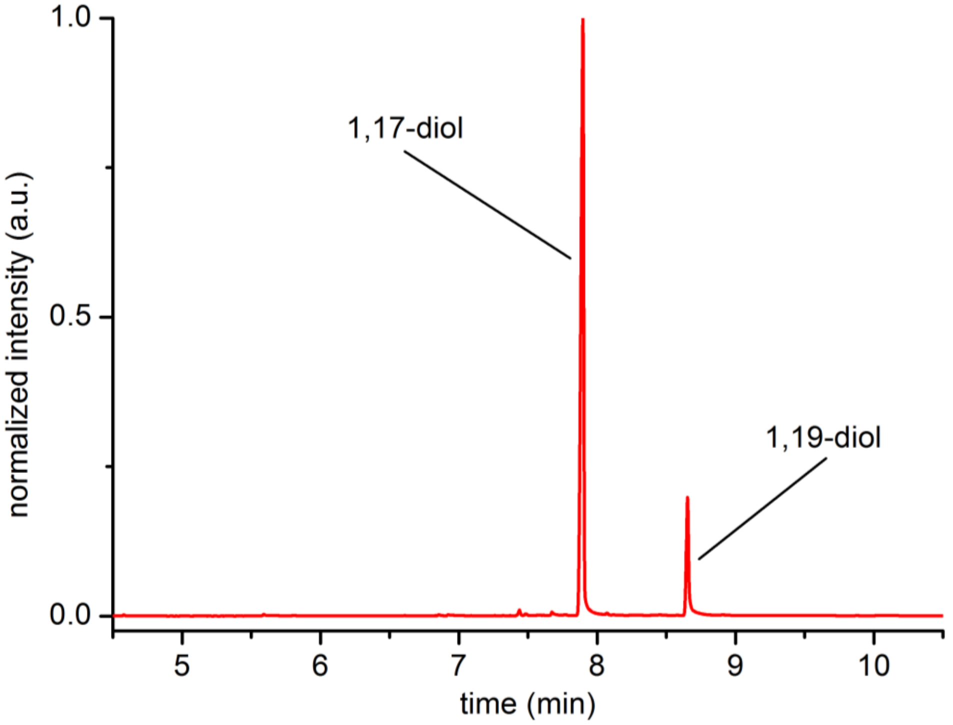


Figure 7.8: GC trace of mixed 1,17- and 1,19-diol after recrystallization from CHCl3.

7.4.6 Synthesis and characterization of mixed linear long-chain Polyester-17/19.17/19

To adjust stoichiometric amounts of diester and diol, average molecular weights were calculated from GC data for the respective monomer. The diester has an average molecular weight of 333.54 g mol^{-1} and the diol of 276.68 g mol^{-1}. Polycondensations were performed under an inert atmosphere in a two neck Schlenk tube, heated with an aluminium block. Temperature was controlled by a thermocouple placed in the block. The polymerization mixture was mechanically stirred with a helical agitator described in more detail in chapter 5.2.1. After weighing the desired amount of monomers into the Schlenk tube, the mixture was degassed and heated to 120 °C. Then 0.1 mL of a 0.008 M solution of $Ti(OBu)_4$ in toluene was added and the temperature was risen by 10 K every 45 minutes. At a temperature of 180 °C vacuum was applied to remove volatiles. The mixture was then stirred overnight at 200 °C under vacuum. The mixed polyester **PE-17/19.17/19** derived from algae oil was analyzed by DSC, ^{1}H NMR and GPC measurements.

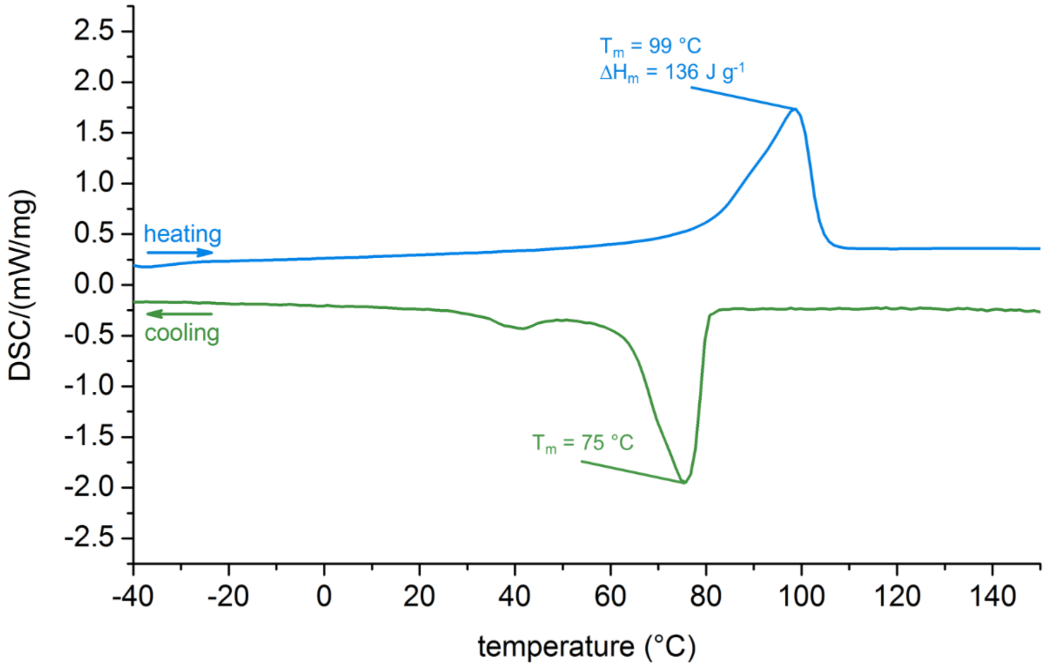
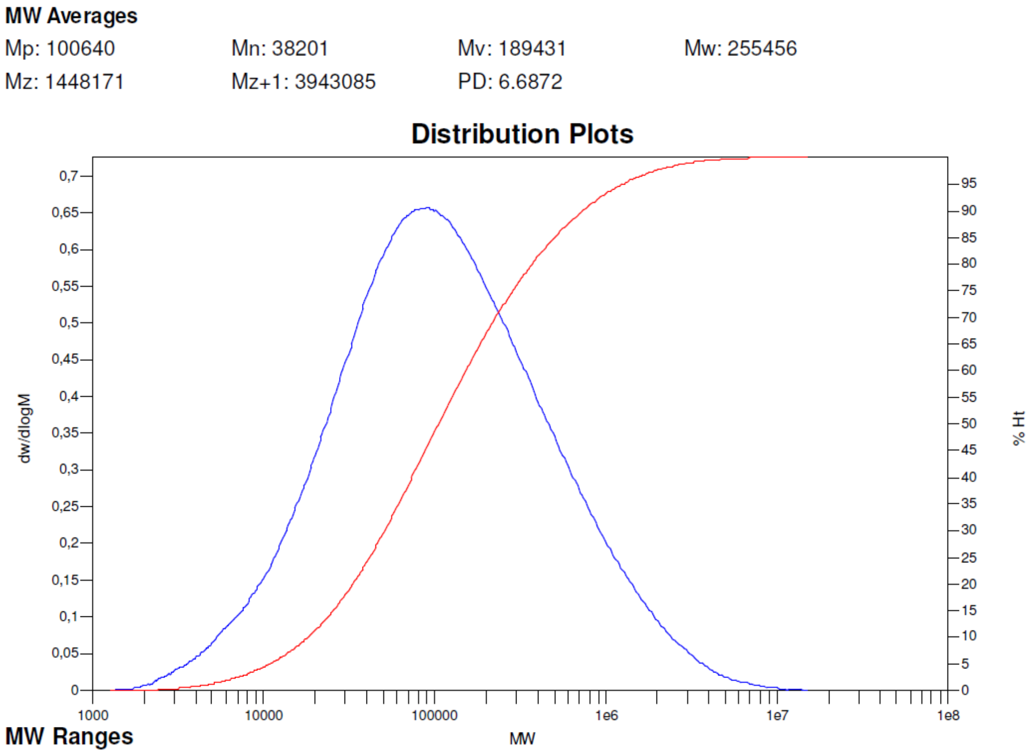


Figure 7.9: DSC trace of mixed polyester **PE-17/19.17/19**.

As determined by DSC mixed linear long-chain polyester **PE-17/19.17/19** exhibits a melting point of T_m 99 °C (T_c = 75 °C, ΔH_m = 136 J g^{-1}). GPC reveals molecular weights M_n of typically 3.8×10^4 g mol^{-1} (M_w/M_n =6.7) (cf. **Figure 7.10**); this data agrees with M_n of 4.2×10^4 g mol^{-1} determined from ^{1}H NMR spectroscopic analysis of the end groups (cf. **Chapter 3.4.3**).


MW Averages

Mp: 100640 Mn: 38201 Mv: 189431 Mw: 255456

Mz: 1448171 Mz+1: 3943085 PD: 6.6872

Figure 7.10: GPC trace of mixed polyester **PE-17/19.17/19**.

Wide-angle X-ray diffraction (WAXD) of this linear long-chain mixed polyester essentially shows the reflexes of the polyethylene portion of the material.

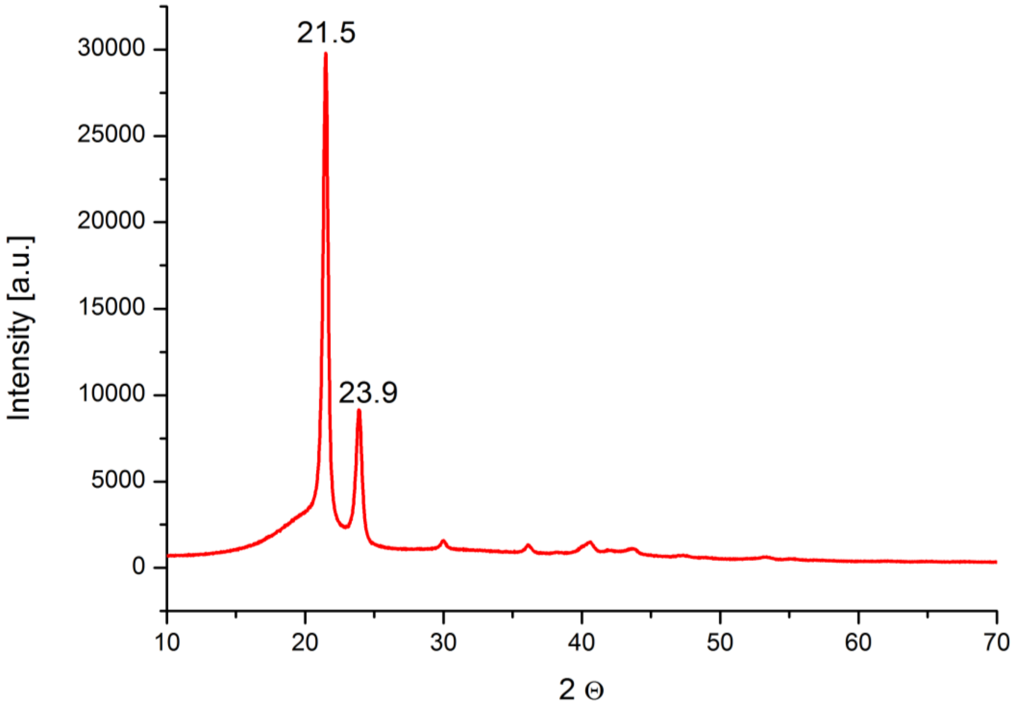
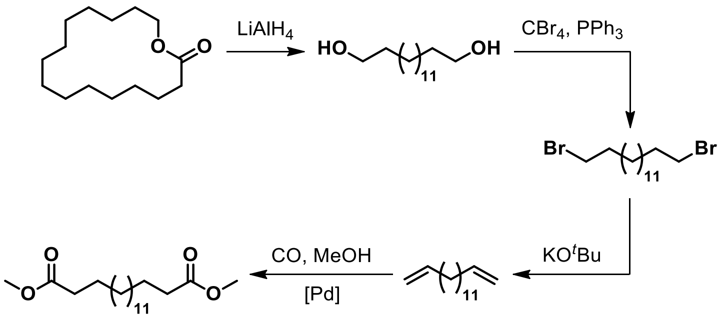


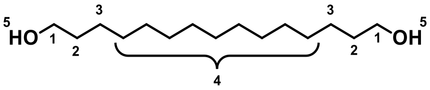
Figure 7.11: WAXD pattern of mixed polyester **PE-17/19.17/19**.

7.4.7 Synthesis of dimethyl-1,17-heptadecanedioate



Pentadecane-1,15-diol[30]

Oxacyclohexadecan-2-one (25.0 g, 104.0 mmol) was dissolved in 60 mL of THF and added dropwise to a cooled suspension (0 °C) of $LiAlH_4$ (8.7 g, 23.0 mmol) in 250 mL of THF. After complete addition, the suspension was refluxed for 1 h and then stirred overnight at room temperature. Then, 50 mL of a 2 M NaOH solution were added, the resulting precipitate was filtered off and washed with 300 mL of THF. Volatiles were removed under reduced pressure and the resulting solid was recrystallized from 300 mL of ethyl acetate, yielding 23.6 g of the desired product (97.0 mmol, 93 %) as a white solid.

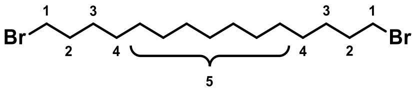


^{1}H NMR ($CDCl_3$, 50 °C, 400 MHz) δ 3.64 (t, $^3J_{H-H}$ = 6.7 Hz, 4H, H-1), 1.57 (quint, $^3J_{H-H}$ = 6.7 Hz, 4H, H-2), 1.40-1.19 (m, 24H, H-3, H-4 and H-5).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 50 °C, 101 MHz) δ 63.3 (C-1), 33.0 (C-2), 29.8-29.6 (C-4), 25.9 (C-3).

1,15-Dibromopentadecane[45]

Pentadecane-1,15-diol (15.0 g, 61.4 mmol) and CBr_4 (52.9 g, 159.6 mmol) were dissolved in 500 mL of methylene chloride and cooled to 0 °C. PPh_3 (44.4 g, 169.4 mmol) was added as solid over a period of 20 minutes. The yellow solution was heated to 45 °C for 4 h and then stirred at room temperature for 17 h. Then 145 mL of methanol and 30 mL of water were added and stirred for 10 min at room temperature. After removal of the solvent a beige solid was obtained which was dissolved in 900 mL of pentane and extracted with methanol (3 x 200 mL). Column chromatography with pure pentane yielded 19.6 g of a white solid (53.0 mmol, 86 %).

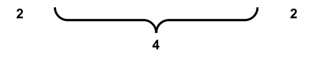


^{1}H NMR ($CDCl_3$, 25 °C, 400 MHz) δ 3.39 (t, $^3J_{H-H}$ = 6.5 Hz, 4H, H-1), 1.84 (quint, $^3J_{H-H}$ = 6.5 Hz, 4H, H-2), 1.47-1.36 (m, 4H, H-3), 1.35-1.21 (m, 18H, H-4 and H-5).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C, 101 MHz) δ 34.1 (C-1), 33.0 (C-2), 29.7-29.6 (C-5), 28.9 (C-4), 28.3 (C-3).

Pentadeca-1,14-diene[46]

1,15-Dibromopentadecane (19.6 g, 53.0 mmol) was dissolved in a mixture of 50 mL of THF and 25 mL of toluene. Addition of KO*t*Bu (12.0 g, 106.0 mmol) in small batches over a 2 h period resulted in a brown suspension. After addition of further 20 mL of THF and 10 mL of toluene, the suspension was stirred at room temperature overnight. Another batch of KO*t*Bu (6.0 g, 53.0 mmol) was then added. After stirring overnight at room temperature 100 mL of water and 100 mL of 1 M HCl were added. The resulting solution was extracted with diethyl ether (3 x 150 mL). The combined organic phases were washed with $NaHCO_3$ (2 x 150 mL) and water (2 x 100 mL) and dried over $MgSO_4$. The solvent was removed in vacuum yielding 11.6 g of the crude product. Column chromatography using pentane as eluent yielded the desired product as colourless liquid. (6.0 g, 28.8 mmol, 54 %).

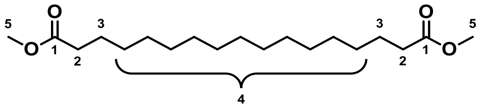


^{1}H NMR ($CDCl_3$, 25 °C, 400 MHz) δ 5.88-5.74 (m, 2H, H-2). 5.03-4.89 (m, 4H, H-1), 2.09-2.00 (m, 4H, H-3), 1.44-1.19 (m, 18H, H-4).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C, 101 MHz) δ 139.4 (C-2), 114.22 (C-1), 34.0 (C-3), 29.8-29.1 (C-4).

Dimethyl-1,17-heptadecanedioate

According to the general methoxycarbonylation procedure, pentadeca-1,14-diene (6.0 g, 28.8 mmol) and [(dtbpx)Pd(OTf)](OTf) (369.0 mg, 0.46 mmol) were mixed with 100 mL of methanol. The resulting biphasic system was transferred into the autoclave. The autoclave was pressurized with 20 bar CO and heated to 90 °C for 3 days while stirring the reaction. The resulting suspension was diluted with methylene chloride and filtered to remove solids. After removing the solvents under reduced pressure, the crude product was recrystallized from methanol to yield the desired product in polycondensation grade purity (3.4 g, 10.3 mmol, 36 %).



^{1}H NMR (CDCl$_3$, 25 °C, 400 MHz) δ 3.66 (s, 6H, H-5), 2.29 (t, $^3J_{H\text{-}H}$ = 7.5 Hz, 4H, H-2), 1.69-1.54 (m, 4H, H-3), 1.38-1.17 (m, 22H, H-4).

^{13}C{^{1}H} NMR (CDCl$_3$, 25 °C, 101 MHz) δ 174.5 (C-1), 51.6 (C-5), 34.3 (C-2), 29.8-29.3 (C-4), 25.1 (C-3).

Elemental analysis for $C_{19}H_{36}O_4$: calculated: 69.47 % C, 11.05 % H, 19.48 % O; found: 69.67 % C, 11.19 % H, 19.14 % O.

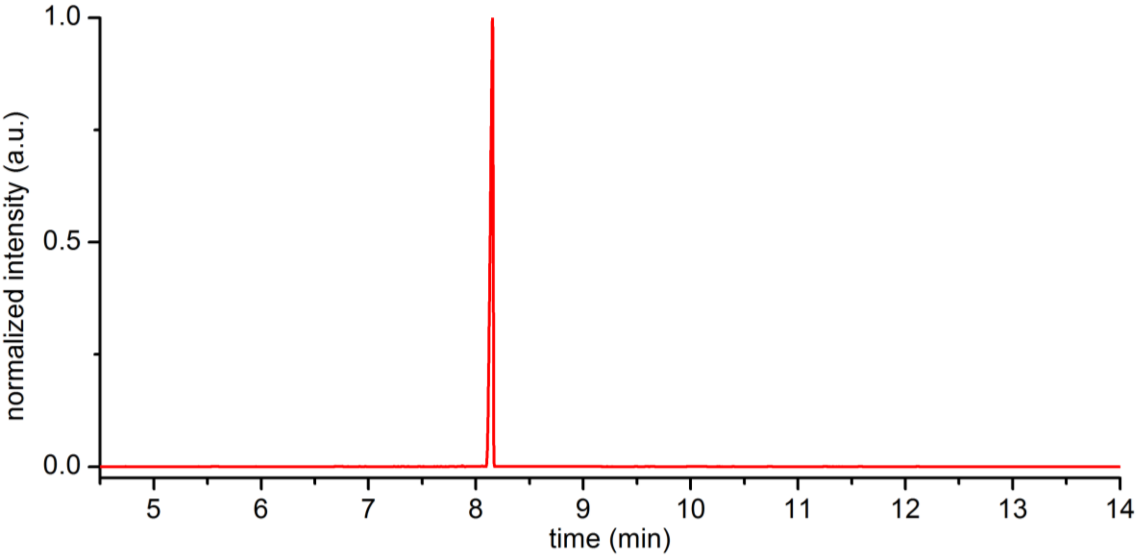
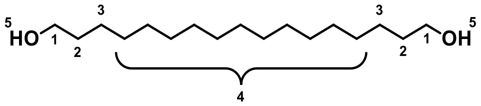


Figure 7.12: GC trace of 1,17-diester after recrystallization from methanol.

Heptadecane-1,17-diol

Dimethyl-1,17-heptadecanedioate (1.68 g, 5.1 mmol) was dissolved in 25 mL of THF and added dropwise to a cooled (0 °C) suspension of LiAlH$_4$ (0.51 g, 13.3 mmol) in 30 mL of THF. After complete addition, the suspension was refluxed for 1 h and then stirred overnight at room temperature. Then, 1.5 mL of water and 0.5 mL of a 2 M NaOH solution were added. The resulting precipitate was filtered off and volatiles were removed under reduced pressure.

Recrystallization of the crude product from $CHCl_3$ yielded 1.20 g of the desired product as a white solid in polycondensation grade purity (4.4 mmol, 86 %).

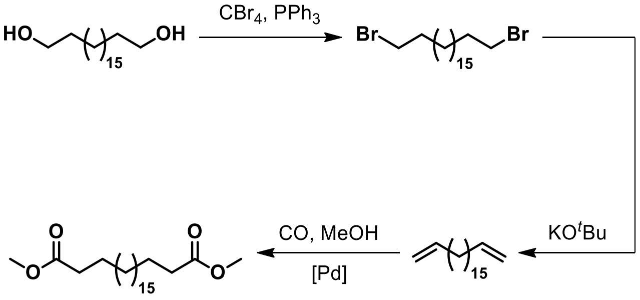


^{1}H NMR ($CDCl_3$, 50 °C, 400 MHz) δ 3.63 (t, $^3J_{H\text{-}H}$ = 6.7 Hz, 4H, H-1), 1.57 (quint, $^3J_{H\text{-}H}$ = 6.7 Hz, 4H, H-2), 1.42-1.25 (m, 26H, H-3, H-4), 1.23 (s, 2H, H-5).

^{13}C{^{1}H} NMR ($CDCl_3$, 50 °C, 101 MHz) δ 63.3 (C-1), 33.1 (C-2), 29.8-29.7 (C-4), 29.6 (C-3).

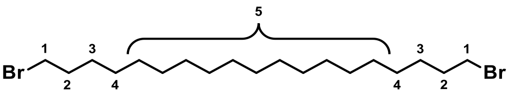
Elemental analysis for $C_{17}H_{36}O_2$: calculated: 74.94 % C, 13.32 % H, 11.74 % O; found: 74.73 % C, 13.45 % H, 11.82 % O.

7.4.8 Synthesis of dimethyl-1,21-henicosanedioate



1,19-Dibromononadecane[45]

Nonadecane-1,19-diol (15.0 g, 49.9 mmol) and CBr_4 (42.4 g, 127.7 mmol) were dissolved in 400 mL of methylene chloride and cooled to 0 °C. PPh_3 (36.2 g, 138.0 mmol) was added as solid over a period of 20 minutes. The yellow solution was then heated to 45 °C for 3 h and then stirred at room temperature overnight. Then 100 mL of methanol and 20 mL of water were added and stirred for 10 min at room temperature. After removal of the solvent a beige solid was obtained, which was dissolved in 400 mL of pentane and extracted with methanol (3 x 100 mL). Column chromatography with pure pentane yielded 18.4 g of a white solid (43.2 mmol, 87 %).

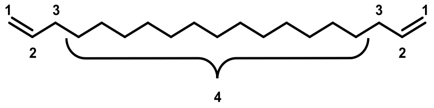


^{1}H NMR ($CDCl_3$, 25 °C, 400 MHz) δ 3.40 (t, $^3J_{H\text{-}H}$ = 6.9 Hz, 4H, H-1), 1.85 (quint, $^3J_{H\text{-}H}$ = 6.9 Hz, 4H, H-2), 1.48-1.35 (m, 4H, H-3), 1.35-1.18 (m, 26H, H-4 and H-5).

^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C, 101 MHz) δ 34.2 (C-1), 33.0 (C-2), 29.8-29.6 (C-5), 28.9 (C-4), 28.3 (C-3).

Nonadeca-1,18-diene[46]

1,19-Dibromononadecan (18.4 g, 43.2 mmol) was dissolved in a mixture of 15 mL of THF and 7.5 mL of toluene. Addition of KO*t*Bu (9.7 g, 86.7 mmol) in small batches over a 1 h period resulted in an orange suspension. After stirring at room temperature overnight, another batch of KO*t*Bu (4.9 g, 43.2 mmol) was added. After stirring overnight at room temperature 30 mL of water and 30 mL of 1 M HCl were added. The resulting solution was extracted with diethyl ether (3 x 50 mL). The combined organic phases were washed with $NaHCO_3$ (2 x 50 mL) and water (2 x 50 mL) and dried over $MgSO_4$. After removing the solvent, the crude product was purified by column chromatography using pentane as eluent. The desired product was obtained as colourless liquid (8.5 g, 32.1 mmol, 74 %).

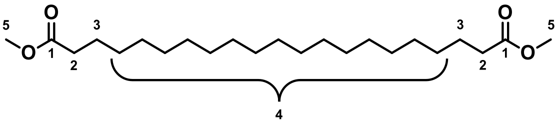


^{1}H NMR ($CDCl_3$, 25 °C, 400 MHz) δ 5.88-5.76 (m, 2H, H-2), 5.03-4.89 (m, 4H, H-1), 2.09-2.00 (m, 4H, H-3), 1.48-1.19 (m, 26H, H-4).

^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C, 101 MHz) δ 139.4 (C-2), 114.2 (C-1), 34.0 (C-3), 29.9-29.1 (C-4).

Dimethyl-1,21-henicosanedioate

According to the general methoxycarbonylation procedure, nonadeca-1,18-diene (8.5 g, 32.1 mmol) and [(dtbpx)Pd(OTf)](OTf) (410.0 mg, 0.51 mmol) were mixed with 120 mL of methanol. The resulting biphasic system was transferred to the autoclave. The autoclave was pressurized with 20 bar CO and heated to 90 °C for 7 days while stirring the reaction. The resulting suspension was diluted with methylene chloride and filtered to remove solids. After removing the solvents under reduced pressure, the crude product was recrystallized from methanol and heptane to yield the desired product in polycondensation grade purity (8.0 g, 20.9 mmol, 65 %).



^{1}H NMR ($CDCl_3$, 25 °C, 400 MHz) δ 3.66 (s, 6H, H-5), 2.29 (t, $^3J_{H\text{-}H}$ = 7.5 Hz, 4H, H-2), 1.61 (quint, $^3J_{H\text{-}H}$ = 7.5, 4H, H-3), 1.39-1.18 (m, 30H, H-4).

^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C, 101 MHz) δ 174.5 (C-1), 51.6 (C-5), 34.3 (C-2), 29.8-29.3 (C-4), 25.1 (C-3).

Elemental analysis for $C_{23}H_{44}O_4$: calculated: 71.83 % C, 11.53 % H, 16.64 % O; found: 71.81 % C, 11.85 % H, 16.34 % O.

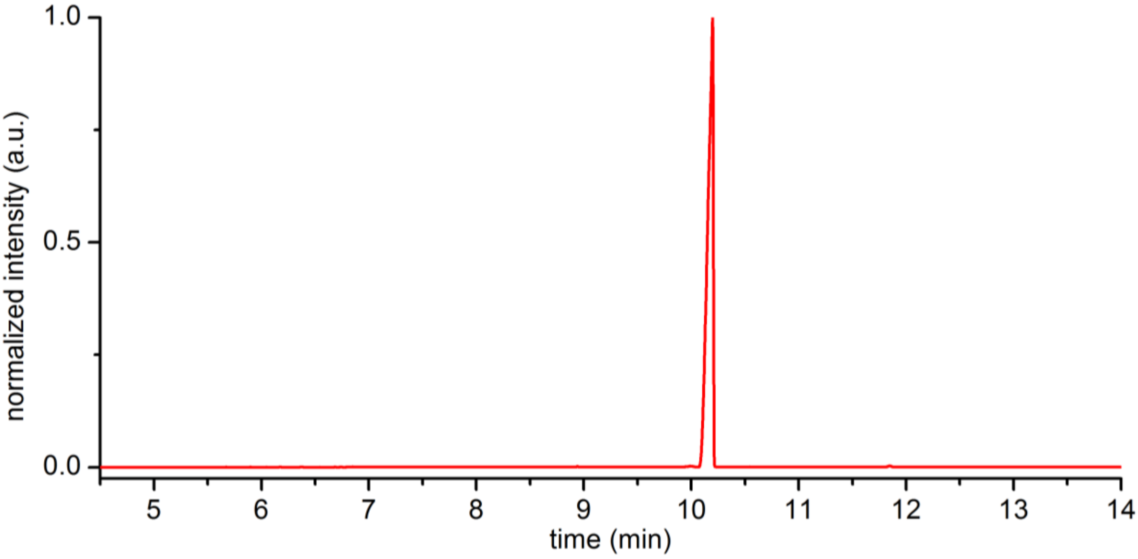
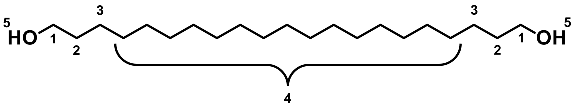


Figure 7.13: GC trace of 1,21-diester after recrystallization from methanol and heptane.

Henicosane-1,21-diol

Dimethyl-1,21-henicosanedioate (5.0 g, 13.0 mmol) was dissolved in 50 mL of THF and added dropwise to a cooled (0 °C) suspension of $LiAlH_4$ (1.32 g, 34.7 mmol) in 80 mL of THF. After complete addition, the suspension was refluxed for 1 h and then stirred at room temperature for 3 days. Then, 4.5 mL of water and 1.5 mL of a 2 M NaOH solution were added. The resulting precipitate was filtered off and volatiles were removed under reduced pressure. Recrystallization of the crude product from $CHCl_3$ yielded 3.4 g of the desired product as a white solid in polycondensation grade purity (10.4 mmol, 80 %).

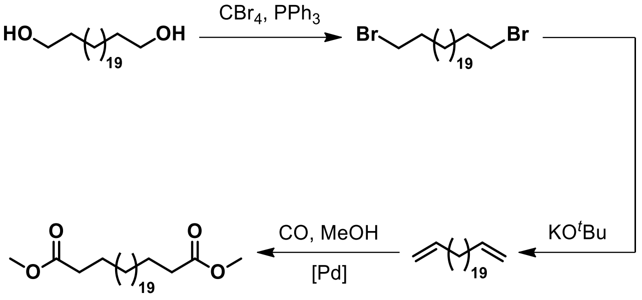


^{1}H NMR ($CDCl_3$, 50 °C, 400 MHz) δ 3.64 (t, $^3J_{H\text{-}H}$ = 6.8 Hz, 4H, H-1), 1.57 (quint, $^3J_{H\text{-}H}$ = 6.8 Hz, 4H, H-2), 1.42-1.24 (m, 34H, H-3 and H-4), 1.20 (s, 2H, H-5).

^{13}C{^{1}H} NMR ($CDCl_3$, 50 °C, 101 MHz) δ 63.3 (C-1), 33.1 (C-2), 29.8-29.8 (C-4), 29.6 (C-3).

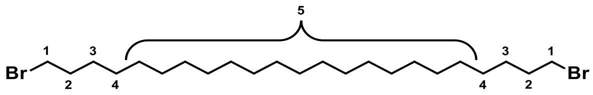
Elemental analysis for $C_{21}H_{44}O_2$: calculated: 76.76 % C, 13.50 % H, 9.74 % O; found: 76.76 % C, 13.44 % H, 9.80 % O.

7.4.9 Synthesis of dimethyl-1,25-pentacosanedioate



1,23-Dibromotricosane[45]

Tricosane-1,23-diol (15.0 g, 42.1 mmol) and CBr4 (35.7 g, 107.8 mmol) were dissolved in 350 mL of methylene chloride and cooled to 0 °C. PPh3 (30.5 g, 116.4 mmol) was added as solid over a period of 20 minutes. The yellow solution was then heated to 45 °C for 3 h and then stirred at room temperature overnight. Then 100 mL of methanol and 20 mL of water were added and stirred for 10 min at room temperature. After removal of the solvent a beige solid was obtained which was dissolved in 400 mL of pentane and extracted with methanol (3 x 100 mL). Recrystallization from ethanol yielded 13.4 g of a white solid (27.8 mmol, 66 %).

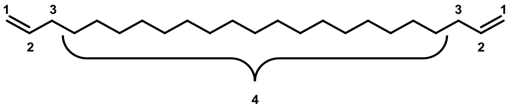


^{1}H NMR (CDCl$_3$, 25 °C, 400 MHz) δ 3.40 (t, $^{3}J_{\text{H-H}}$ = 6.9 Hz, 4H, H-1), 1.85 (quint, $^{3}J_{\text{H-H}}$ = 6.9 Hz, 4H, H-2), 1.48-1.35 (m, 4H, H-3), 1.41-1.21 (m, 34H, H-4, H-5).

^{13}C{^{1}H} NMR (CDCl$_3$, 25 °C, 101 MHz) δ 34.2 (C-1), 33.0 (C-2), 30.0-29.4 (C-5), 28.9 (C-4), 28.3 (C-3).

Tricosa-1,22-diene[46]

1,23-Dibromotricosane (13.3 g, 27.5 mmol) was dissolved in a mixture of 30 mL of THF and 15 mL of toluene. Addition of KO*t*Bu (6.2 g, 55.2 mmol) in small batches over a 1 h period resulted in an orange suspension. After stirring at room temperature overnight, another batch of KO*t*Bu (3.1 g, 27.6 mmol) was added and the reaction mixture was stirred for another night at room temperature. Then the reaction was quenched by addition of 30 mL of water and 30 mL of 1 M HCl. The resulting solution was extracted with diethyl ether (3 x 50 mL). The combined organic phases were washed with NaHCO$_3$ (2 x 50 mL) and water (2 x 50 mL) and dried over MgSO$_4$. After removing the solvent, the crude product was purified by column chromatography using pentane as eluent. The desired product was obtained as colourless liquid (6.7 g, 21.0 mmol, 76 %).

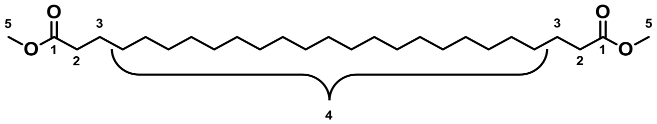


^{1}H NMR (CDCl$_3$, 25 °C, 400 MHz) δ 5.87-5.76 (m, 2H, H-2). 5.02-4.91 (m, 4H, H-1), 2.07-2.01 (m, 4H, H-3), 1.49-1.20 (m, 34H, H-4).

^{13}C{^{1}H} NMR (CDCl$_3$, 25 °C, 101 MHz) δ 139.4 (C-2), 114.2 (C-1), 34.0 (C-3), 29.9-29.7 (C-4).

Dimethyl-1,25-pentacosanedioate

According to the general methoxycarbonylation procedure, tricosa-1,22-diene (5.0 g, 15.6 mmol) and [(dtbpx)Pd(OTf)](OTf) (199.4 mg, 0.25 mmol) were mixed with 160 mL of methanol. The resulting biphasic system was transferred to the autoclave. The autoclave was pressurized with 20 bar CO and heated to 90 °C for 7 days while stirring the reaction. The resulting suspension was diluted with methylene chloride and filtered to remove solids. After removing the solvents under reduced pressure, the crude product was recrystallized from methanol and heptane to yield the desired product in polycondensation grade purity (6.0 g, 13.5 mmol, 87 %).



^{1}H NMR (CDCl$_3$, 25 °C, 400 MHz) δ 3.66 (s, 6H, H-5), 2.29 (t, $^{3}J_{H\text{-}H}$ = 7.4 Hz, 4H, H-2), 1.61 (quint, $^{3}J_{H\text{-}H}$ = 7.4, 4H, H-3), 1.34-1.20 (m, 38H, H-4).

^{13}C{^{1}H} NMR (CDCl$_3$, 25 °C, 101 MHz) δ 174.5 (C-1), 51.6 (C-5), 34.3 (C-2), 29.8-29.3 (C-4), 25.1 (C-3).

Elemental analysis for $C_{27}H_{52}O_4$: calculated: 73.59 % C, 11.89 % H, 14.52 % O; found: 73.71 % C, 11.77 % H, 14.52 % O.

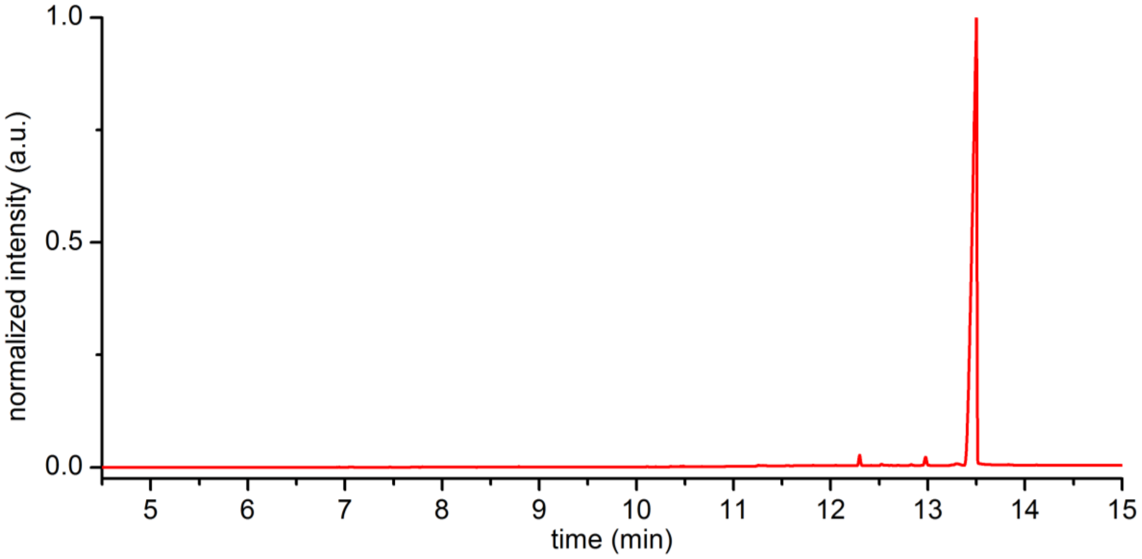
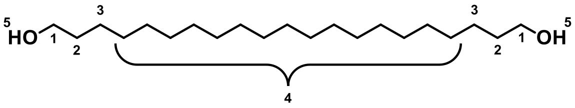


Figure 7.14: GC trace of 1,25-diester after recrystallization from methanol and heptane.

Pentacosane-1,25-diol

The reduction was carried out analogous to a reported procedure[32] in a 300 mL stainless steel mechanically stirred pressure reactor equipped with a heating jacket and a glass inlay. Prior to the reduction experiment the reactor was purged several times with argon. Dimethyl-1,25-pentacosanedioate (9.0 mmol, 4.0 g) was weighed under air into a dry Schlenk tube equipped with a magnetic stir bar, which was then purged several times with argon. Dry and degassed THF (40 mL) was added using standard Schlenk techniques. Vigorous stirring afforded a homogeneous reaction mixture. In the glovebox dichlorobis[2-(diphenylphosphino)ethylamine] ruthenium (16.8 µmol, 10 mg) and sodium methanolate (1.1 mmol, 60 mg) were weighed into a dry Schlenk tube equipped with a magnetic stir bar. After the Schlenk tube was removed from the glovebox, 40 mL of dry and degassed THF were added. Both mixtures were then cannula-transferred into the reactor in an argon counter stream. The reactor was closed, pressurized with 50 bar hydrogen and then heated to 100 °C for 22 h. After cooling to room temperature, the reactor was vented. The reaction mixture was removed from the reactor and heated to 50 °C to remove catalyst residues by filtration over a Buchner funnel. Removing the solvent in vacuum and recrystallization from chloroform yielded pentacosane-1,25-diol (2.7 g, 7.0 mmol, 78 %).



^{1}H NMR (CDCl$_3$, 50 °C, 400 MHz) δ 3.64 (t, $^3J_{H\text{-}H}$ = 6.8 Hz, 4H, H-1), 1.57 (quint, $^3J_{H\text{-}H}$ = 6.8 Hz, 4H, H-2), 1.40-1.24 (m, 42H, H-3, H-4), 1.20 (s, 2H, H-5).

^{13}C{^{1}H} NMR (CDCl$_3$, 50 °C, 101 MHz) δ 63.3 (C-1), 33.1 (C-2), 29.9-29.6 (C-3), 26.0 (C-3`).

Elemental analysis for $C_{25}H_{52}O_2$: calculated: 78.06 % C, 13.63 % H, 8.32 % O; found: 78.01 % C, 13.88 % H, 8.11 % O.

7.4.10 Synthesis and characterization of Polyester-17.17, Polyester-21.21 and Polyester-25.25

Polyesters were prepared in a 100 mL two-necked Schlenk tube equipped with an overhead stirrer. Efficient mixing of the highly viscous polymer melt was achieved by a helical agitator described in more detail in chapter 5.2.1. Under a static argon atmosphere the monomers (3.25 mmol of the α,ω-diester, respectively, and 3.25 mmol of the corresponding α,ω-diol) were filled into the reaction vessel and molten by heating to 120 °C. A 1.2 mL aliquot of a 0.28 M titanium(IV) butoxide solution in toluene was injected, and the temperature was raised to 200 °C over the course of 8 h. Finally, the polymer melt was stirred overnight at this temperature under reduced pressure (0.01 mbar). Polyesters were analysed by DSC, ^{1}H NMR and GPC measurements.

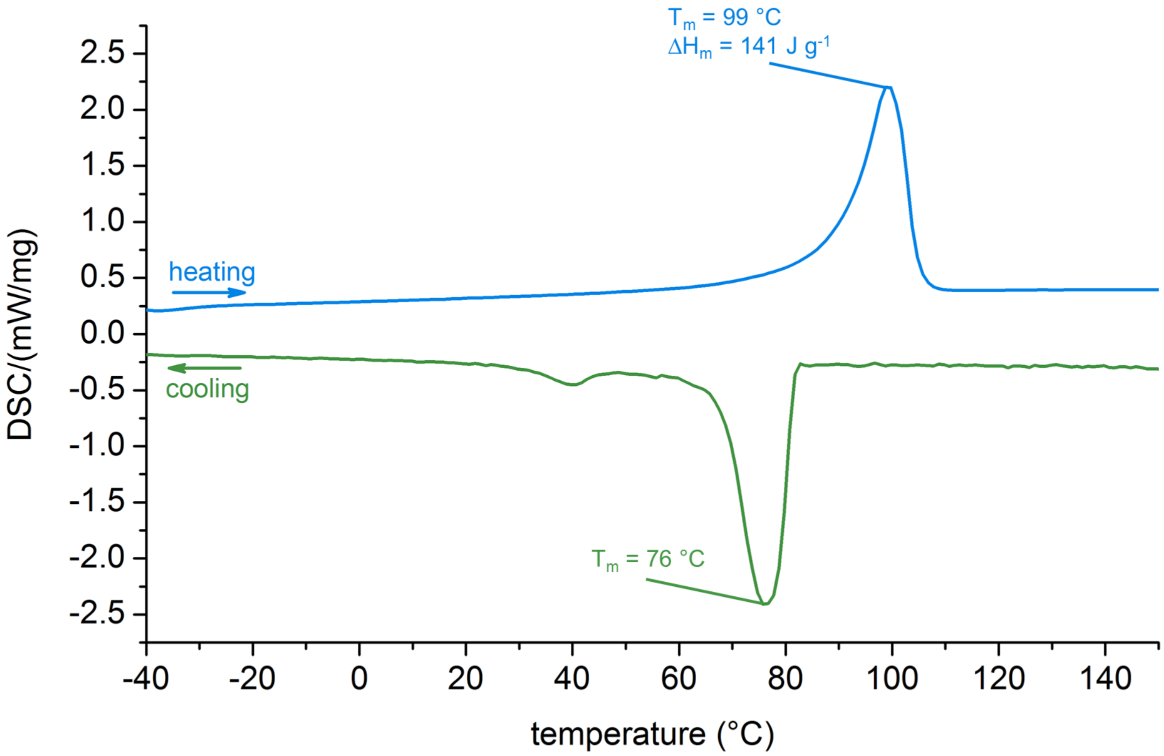


Figure 7.15: DSC trace of poly[1,17-heptadecanediyl-1,17-heptadecanedioate].

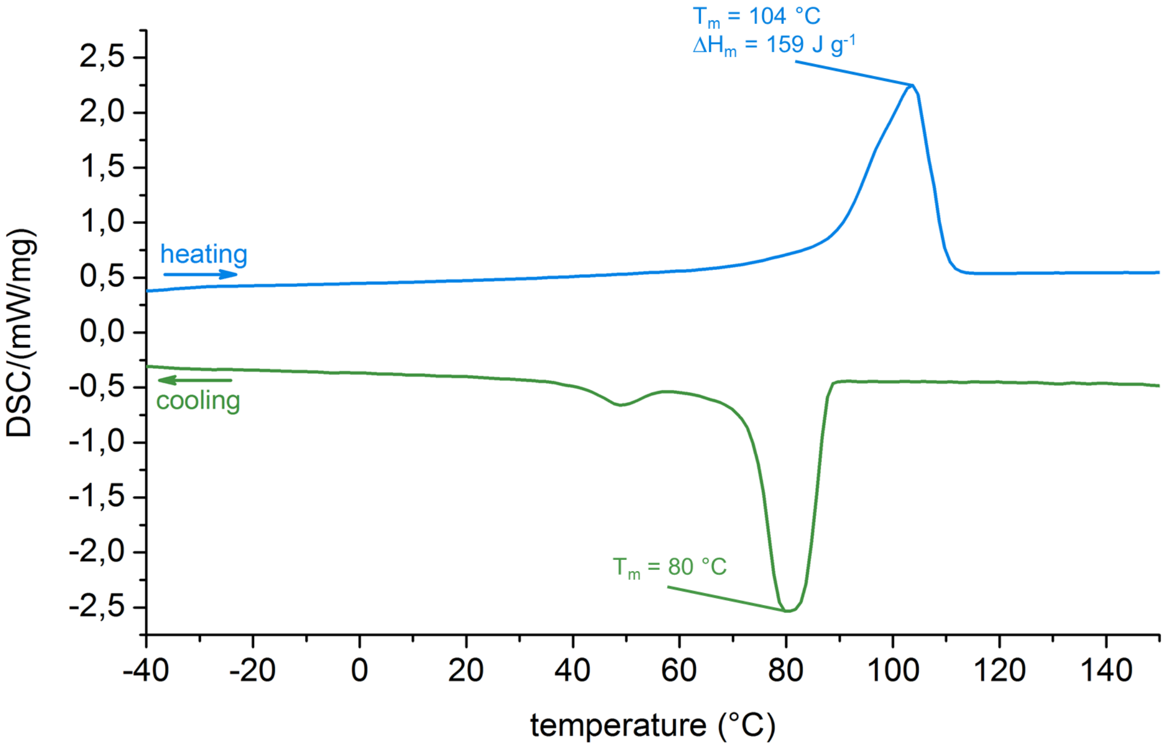


Figure 7.16: DSC trace of poly[1,21-henicosanediyl-1,21-henicosanedioate].

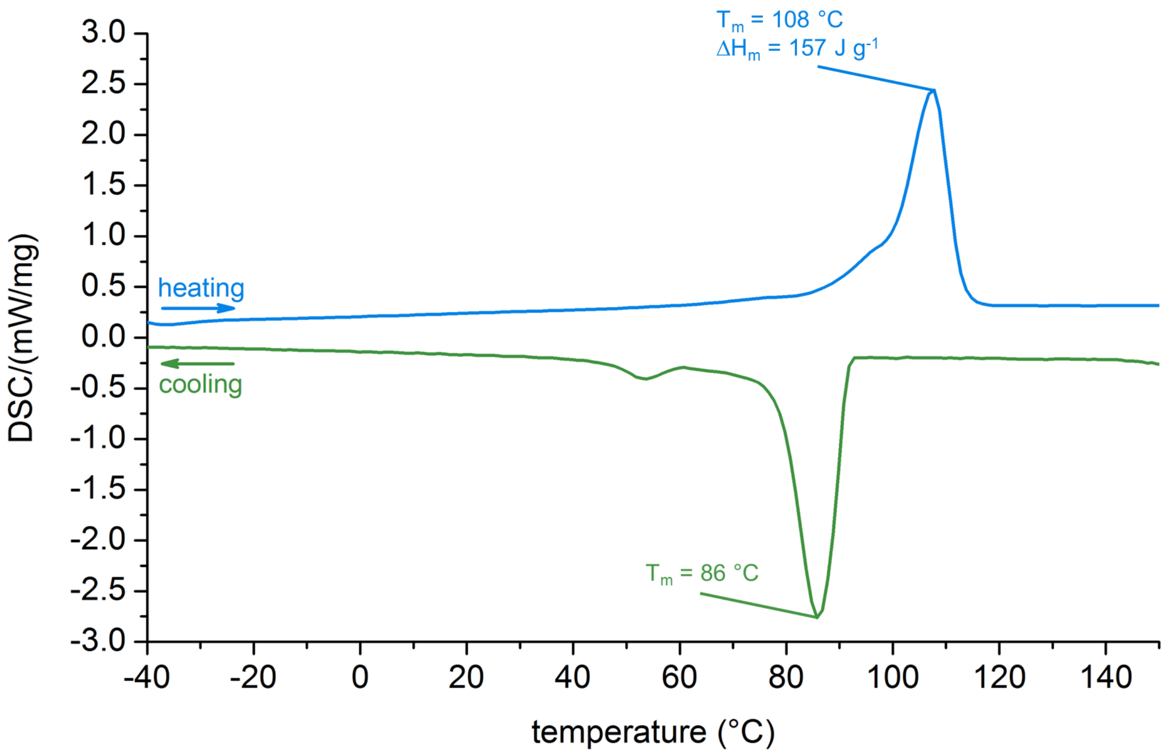
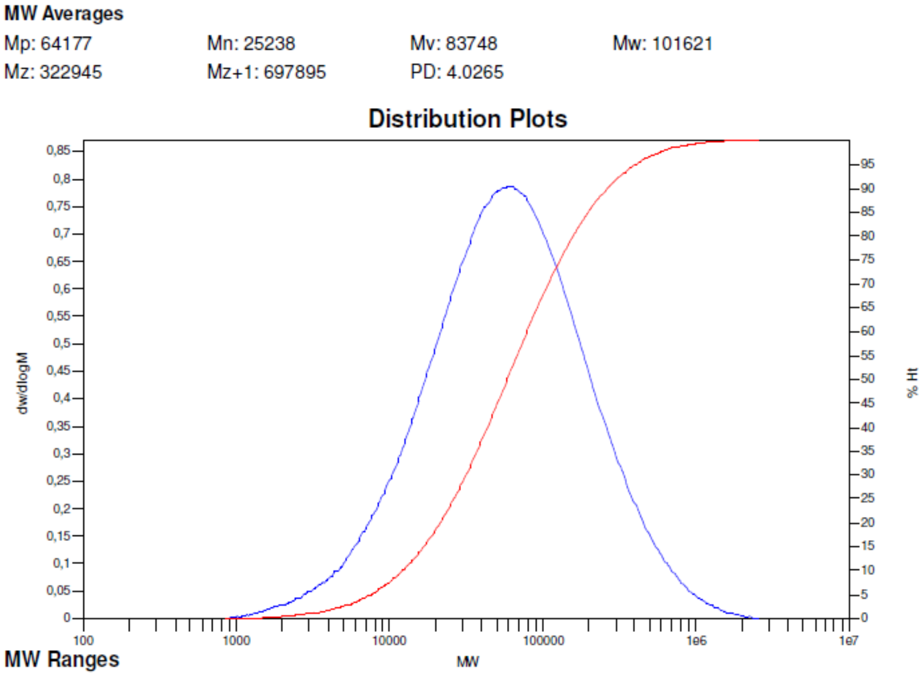


Figure 7.17: DSC trace of poly[1,25-pentacosanediyl-1,25-pentacosanedioate].

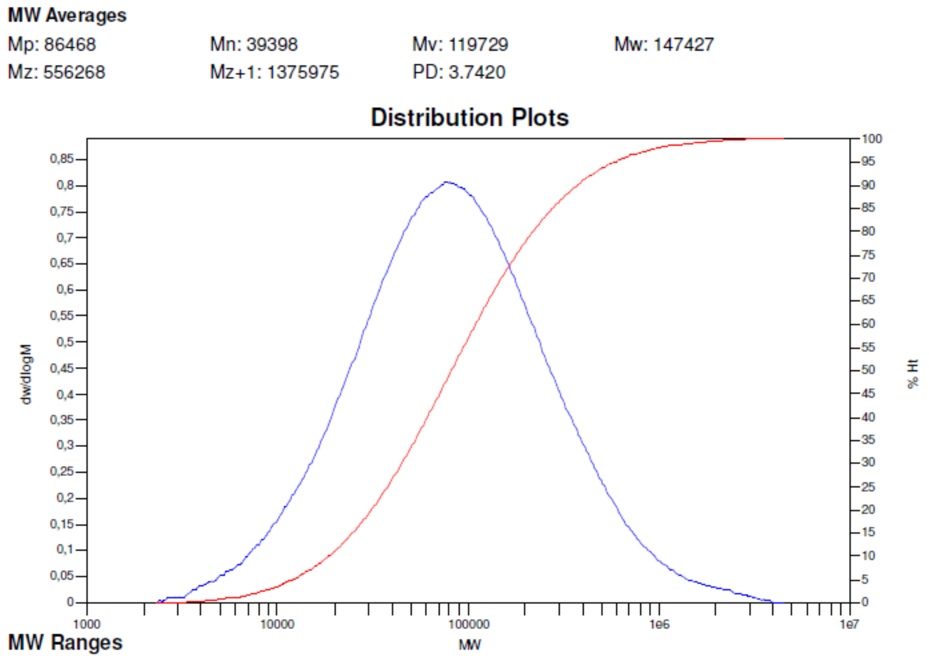


MW Averages

Mp: 64177 Mn: 25238 Mv: 83748 Mw: 101621

Mz: 322945 Mz+1: 697895 PD: 4.0265

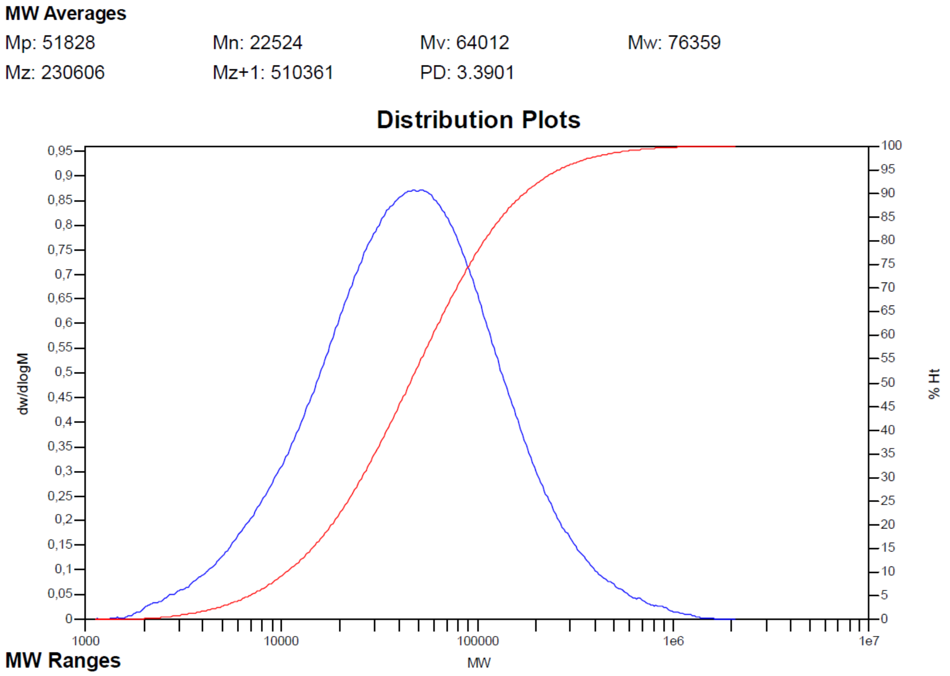
Figure 7.18: GPC trace of poly[1,17-heptadecanediyl-1,17-heptadecanedioate].



MW Averages

Mp: 86468
Mn: 39398
Mv: 119729
Mw: 147427
Mz: 556268
Mz+1: 1375975
PD: 3.7420

Figure 7.19: GPC trace of poly[1,21-henicosanediyl-1,21-henicosanedioate].



MW Averages

Mp: 51828
Mn: 22524
Mv: 64012
Mw: 76359
Mz: 230606
Mz+1: 510361
PD: 3.3901

Figure 7.20: GPC trace of poly[1,25-pentacosanediyl-1,25-pentacosanedioate].

7.5 References

1. Impact Assessment of the European Biofuel Directive on Land Use and Biodiversity. Hellmann, F.; Verburg, P. H. *J. Environ. Manage.* **2010**, *91*, 1389-1396.
2. The Place of Algae in Agriculture: Policies for Algal Biomass Production. Trentacoste, E.; Martinez, A.; Zenk, T. *Photosynth. Res.* **2014**, 1-11.
3. Biodiesel from Microalgae. Chisti, Y. *Biotechnol. Adv.* **2007**, *25*, 294-306.
4. Microalgae for Biodiesel Production and Other Applications: A Review. Mata, T. M.; Martins, A. A.; Caetano, N. S. *Renew. Sust. Energ. Rev.* **2010**, *14*, 217-232.
5. Gold Rush for Algae. Mascarelli, A. L. *Nature* **2009**, *461*, 460-461.
6. Algae as a Source of Renewable Chemicals: Opportunities and Challenges. Foley, P. M.; Beach, E. S.; Zimmerman, J. B. *Green Chem.* **2011**, *13*, 1399-1405.
7. Green Chemistry and the Ocean-Based Biorefinery. Kerton, F. M.; Liu, Y.; Omari, K. W.; Hawboldt, K. *Green Chem.* **2013**, *15*, 860-871.
8. Composition of Algal Oil and Its Potential as Biofuel. Schlagermann, P.; Göttlicher, G.; Dillschneider, R.; Rosello-Sastre, R.; Posten, C. *J. Combust.* **2012**, *2012*, 1-14.
9. Catalytic Deoxygenation of Microalgae Oil to Green Hydrocarbons. Zhao, C.; Bruck, T.; Lercher, J. A. *Green Chem.* **2013**, *15*, 1720-1739.
10. Lipids and Lipid Metabolism in Eukaryotic Algae. Guschina, I. A.; Harwood, J. L. *Progr. Lipid Res.* **2006**, *45*, 160-186.
11. Long Chain Polyunsaturated Fatty Acid Production and Partitioning to Triacylglycerols in Four Microalgae. Tonon, T.; Harvey, D.; Larson, T. R.; Graham, I. A. *Phytochemistry* **2002**, *61*, 15-24.
12. Fatty Acid Composition of 12 Microalgae for Possible Use in Aquaculture Feed. Patil, V.; Källqvist, T.; Olsen, E.; Vogt, G.; Gislerød, H. *Aquacult Int.* **2007**, *15*, 1-9.
13. Diatoms: A Fossil Fuel of the Future. Levitan, O.; Dinamarca, J.; Hochman, G.; Falkowski, P. G. *Trends Biotechnol.* **2014**, *32*, 117-124.
14. Primary Productivity of Planet Earth: Biological Determinants and Physical Constraints in Terrestrial and Aquatic Habitats. Geider, R. J.; Delucia, E. H.; Falkowski, P. G.; Finzi, A. C.; Grime, J. P.; Grace, J.; Kana, T. M.; La Roche, J.; Long, S. P.; Osborne, B. A.; Platt, T.; Prentice, I. C.; Raven, J. A.; Schlesinger, W. H.; Smetacek, V.; Stuart, V.; Sathyendranath, S.; Thomas, R. B.; Vogelmann, T. C.; Williams, P.; Woodward, F. I. *Glob. Change Biol.* **2001**, *7*, 849-882.
15. The Phaeodactylum Genome Reveals the Evolutionary History of Diatom Genomes. Bowler, C.; Allen, A. E.; Badger, J. H.; Grimwood, J.; Jabbari, K.; Kuo, A.; Maheswari, U.;

Martens, C.; Maumus, F.; Otillar, R. P.; Rayko, E.; Salamov, A.; Vandepoele, K.; Beszteri, B.; Gruber, A.; Heijde, M.; Katinka, M.; Mock, T.; Valentin, K.; Verret, F.; Berges, J. A.; Brownlee, C.; Cadoret, J.-P.; Chiovitti, A.; Choi, C. J.; Coesel, S.; De Martino, A.; Detter, J. C.; Durkin, C.; Falciatore, A.; Fournet, J.; Haruta, M.; Huysman, M. J. J.; Jenkins, B. D.; Jiroutova, K.; Jorgensen, R. E.; Joubert, Y.; Kaplan, A.; Kroger, N.; Kroth, P. G.; La Roche, J.; Lindquist, E.; Lommer, M.; Martin-Jezequel, V.; Lopez, P. J.; Lucas, S.; Mangogna, M.; McGinnis, K.; Medlin, L. K.; Montsant, A.; Secq, M.-P. O.-L.; Napoli, C.; Obornik, M.; Parker, M. S.; Petit, J.-L.; Porcel, B. M.; Poulsen, N.; Robison, M.; Rychlewski, L.; Rynearson, T. A.; Schmutz, J.; Shapiro, H.; Siaut, M.; Stanley, M.; Sussman, M. R.; Taylor, A. R.; Vardi, A.; von Dassow, P.; Vyverman, W.; Willis, A.; Wyrwicz, L. S.; Rokhsar, D. S.; Weissenbach, J.; Armbrust, E. V.; Green, B. R.; van de Peer, Y.; Grigoriev, I. V. *Nature* **2008**, *456*, 239-244.

16. Kroth, P. in *Protein Targeting Protocols, Vol. 390* (Ed: Giezen, M.), Humana Press, **2007**, pp. 257-267.
17. Anneken, D. J.; Both, S.; Christoph, R.; Fieg, G.; Steinberner, U.; Westfechtel, A. in *Ullmann's Encyclopedia of Industrial Chemistry, Vol. 14* (Eds: Gerhartz, W.; Elver, B.), Wiley-VCH, Weinheim, **2000**, pp. 73-116.
18. Fette und Öle als Nachwachsende Rohstoffe in der Chemie. Biermann, U.; Bornscheuer, U.; Meier, M. A. R.; Metzger, J. O.; Schäfer, H. J. *Angew. Chem. Int. Ed.* **2011**, *50*, 3854-3871.
19. Refining of Plant Oils to Chemicals by Olefin Metathesis. Chikkali, S.; Mecking, S. *Angew. Chem. Int. Ed.* **2012**, *51*, 5802-5808.
20. R. Goss, C. Wilhelm, in *Lipids in Photosynthesis, Vol. 30* (Eds: H. Wada, N. Murata), Springer Netherlands, **2010**, pp. 117-137.
21. A Simple Method for the Isolation and Purification of Total Lipides from Animal Tissues. Folch, J.; Lees, M.; Stanley, G. H. S. *J. Biol. Chem.* **1957**, *226*, 497-509.
22. A Comparison of Five Lipid Extraction Solvent Systems for Lipidomic Studies of Human LDL. Reis, A.; Rudnitskaya, A.; Blackburn, G. J.; Fauzi, N. M.; Pitt, A. R.; Spickett, C. M. *J. Lipid Res.* **2013**, *54*, 1812-1824.
23. Common nomenclature of fatty acids gives the number of carbon atoms in the fatty acid chain and the number of double bonds.
24. Oligomeric PEG-Phospholipids for Solubilization and Stabilization of Fluorescent Nanocrystals in Water. Travert-Branger, N.; Dubois, F.; Carion, O.; Carrot, G.; Mahler, B.; Dubertret, B.; Doris, E.; Mioskowski, C. *Langmuir* **2008**, *24*, 3016-3019.

25. Dicarboxylic Acid Esters from the Carbonylation of Unsaturated Esters under Mild Conditions. Jiménez-Rodriguez, C.; Eastham, G. R.; Cole-Hamilton, D. J. *Inorg. Chem. Commun.* **2005**, *8*, 878-881.
26. Linear Semicrystalline Polyesters from Fatty Acids by Complete Feedstock Molecule Utilization. Quinzler, D.; Mecking, S. *Angew. Chem. Int. Ed.* **2010**, *49*, 4306-4308.
27. Mechanistic Features of Isomerizing Alkoxycarbonylation of Methyl Oleate. Roesle, P.; Dürr, C. J.; Möller, H. M.; Cavallo, L.; Caporaso, L.; Mecking, S. *J. Am. Chem. Soc.* **2012**, *134*, 17696-17703.
28. Polymerisable Di- and Triesters from Tall Oil Fatty Acids and Related Compounds. Furst, M. R. L.; Seidensticker, T.; Cole-Hamilton, D. J. *Green Chem.* **2013**, *15*, 1218-1225.
29. Changes in the Chemical Composition of Essential oil of Angelica archangelica L. roots during storage. Nivinskiene, O.; Butkiene, R.; Mockute, D. Chemija **2003**, *14*, 52-56.
30. Enzyme-Catalyzed Hydrolysis of 18-Methyl Eicosanoic Acid-Cysteine Thioester. Ganske, F.; Meyer, H. H.; Deutz, H.; Bornscheuer, U. *Eur. J. Lipid Sci. Tech.* **2003**, *105*, 627-632.
31. A Comprehensive Mechanistic Picture of the Isomerizing Alkoxycarbonylation of Plant Oils. Roesle, P.; Caporaso, L.; Schnitte, M.; Goldbach, V.; Cavallo, L.; Mecking, S. *J. Am. Chem. Soc.* **2014**, *136*, 16871-16881.
32. Dihydrogen Reduction of Carboxylic Esters to Alcohols under the Catalysis of Homogeneous Ruthenium Complexes: High Efficiency and Unprecedented Chemoselectivity. Saudan, L. A.; Saudan, C. M.; Debieux, C.; Wyss, P. *Angew. Chem. Int. Ed.* **2007**, *46*, 7473-7476.
33. Polymers and Polyfunctionality. Carothers, W. H. *Trans. Faraday Soc.* **1936**, *32*, 39-49.
34. This typical nomenclature of polyesters designates the number of carbon atoms in the dicarboxylic acid and the diol monomer component, respectively.
35. Encoding Crystal Microstructure and Chain Folding in the Chemical Structure of Synthetic Polymers. De Ten Hove, C. L. F.; Penelle, J.; Ivanov, D. A.; Jonas, A. M. *Nat. Mater.* **2004**, *3*, 33-37.
36. Characterization of Long-Chain Aliphatic Polyesters: Crystalline and Supramolecular Structure of PE22,4 Elucidated by X-ray Scattering and Nuclear Magnetic Resonance. Menges, M. G.; Penelle, J.; Le Fevere de Ten Hove, C.; Jonas, A. M.; Schmidt-Rohr, K. *Macromolecules* **2007**, *40*, 8714-8725.
37. From Polyethylene to Polyester: Influence of Ester Groups on the Physical Properties. Pepels, M. P. F.; Hansen, M. R.; Goossens, H.; Duchateau, R. *Macromolecules* **2013**, *46*, 7668-7677.

38. Long-Spaced Aliphatic Polyesters. Ortmann, P.; Mecking, S., *Macromolecules* **2013**, *46*, 7213-7218.
39. Which Polyesters Can Mimic Polyethylene? Stempfle, F.; Ortmann, P.; Mecking, S. *Macromol. Rapid Commun.* **2013**, *34*, 47-50.
40. a) Korshak, V. V.; Vinogradova, S. V. *Polyesters*; Pergamon Press: Oxford, U.K., **1965**. b) Mandelkern, L.; Alamo, R. G. in *Physical Properties of Polymers Handbook*; Ed. Mark, J. E.; Springer: New York, **2007**; pp 165-186. c) Renewable Resource-Based Poly(dodecyloate) by Carbonylation Polymerization. Quinzler, D.; Mecking, S. *Chem. Commun.* **2009**, *36*, 5400-5402. d) Yamamoto, M.; Witt, U.; Skupin, G.; Beimborn, D.; Müller R.-J. in *Biopolymers*; Eds. Steinbüchel, A.; Doi, Y. Wiley-VCH: Weinheim, **2002**; Vol. 4, pp 299-311. e) Crystallization in High Polymers. V. Dependence of Melting Temperatures of Polyesters and Polyamides on Composition and Molecular Weight. Evans, R. D.; Mighton, H. R.; Flory, P. J. *J. Am. Chem. Soc.* **1950**, *72*, 2018-2028.
41. Epitaxial Crystallization of Polyesters on Inorganic and Organic Substrates. Rickert, S. E.; Baer, E.; Wittmann, J. C.; Kovacs, A. J. *J. Polym. Sci.; Phys. Ed.* **1978**, *16*, 895-906.
42. Long-Chain Linear C_{19} and C_{23} Monomers and Polycondensates from Unsaturated Fatty Acid Esters. Stempfle, F.; Quinzler, D.; Heckler, I.; Mecking, S. *Macromolecules* **2011**, *44*, 4159-4166.
43. Studies of Marine Planktonic Diatoms: I. Cyclotella Nana Hustedt, and Detonula Confervacea (Cleve) Gran. Guillard, R. R. L.; Ryther, J. H. Can. *J. Microbiol.* **1962**, *8*, 229-239.
44. Guillard, R. L. in *Culture of Marine Invertebrate Animals*, (Eds Smith, W. L.; Chanley, M. H.), Springer US, **1975**, pp. 29-60.
45. Decreasing the Alkyl Branch Frequency in Precision Polyethylene: Pushing the Limits toward Longer Run Lengths. Inci, B.; Wagener, K. B. *J. Am. Chem. Soc.* **2011**, *133*, 11872-11875.
46. Renewable Polyethylene Mimics Derived from Castor Oil. Türünç, O.; Montero de Espinosa, L.; Meier, M. A. R. *Macromol. Rapid Comm.* **2011**, *32*, 1357-1361.

8 Conclusive summary

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. In view of the limited range of these fossil feedstocks alternative renewable resource-based polymers are desirable on the long term. Moreover, providing that the unique molecular structure of these alternative resources can be carried over into the resulting polymers, the utilization of alternative feedstocks can give access to novel useful material property profiles. This, however, requires the efficient transformation of these substrates into useful building blocks.

Fatty acids from plant oils are attractive starting materials in this respect. They contain linear long-chain hydrocarbon segments that can provide e.g. crystallinity and corresponding thermal properties, as well as, a relatively high hydrophobicity. Conversion of these substrates into α,ω-difunctional compounds, which amongst others can serve as monomers for long-chain aliphatic polycondensates, can be achieved by biotechnological approaches such as ω-oxidation or ω-hydroxylation.

Alternatives to these biotechnological routes, which suffer from limitations concerning the effort for work-up, purity of the monomers and cost of the carbohydrate feedstock required, based on chemical catalysis have emerged more recently. Self-metathesis of unsaturated fatty acids by ruthenium alkylidenes for example yields even carbon number monounsaturated diacids,[1] which can be converted to the saturated analogues by hydrogenation of the double bond (**Figure 8.1**).

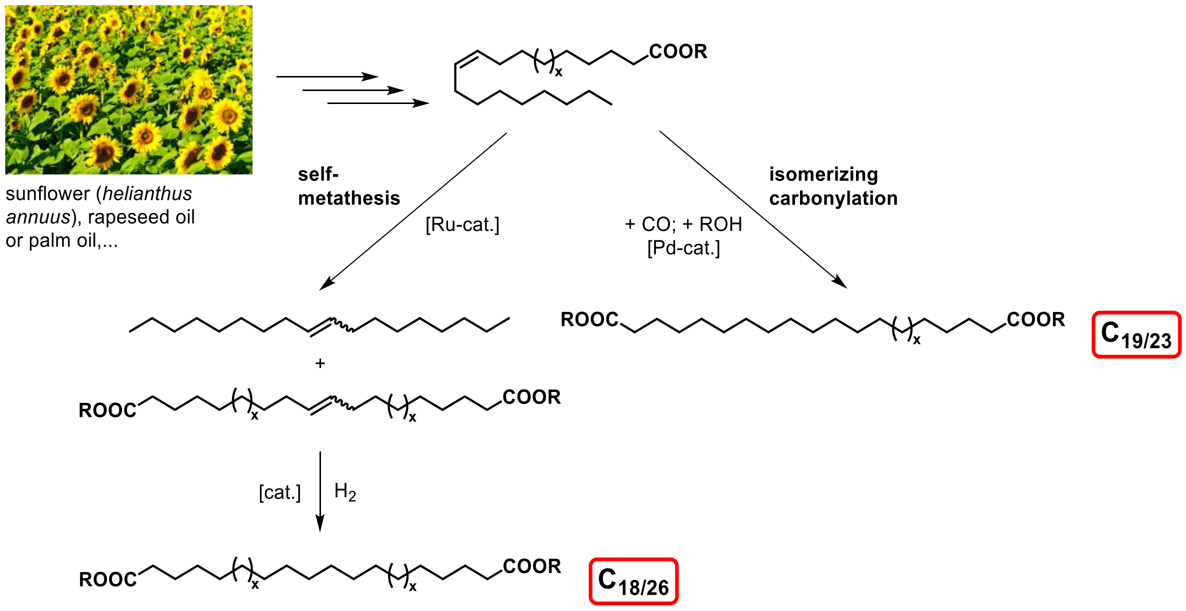


Figure 8.1: Chemical routes to α,ω-difunctional linear monomers based on different fatty acids (x = 1: oleic acid; x = 5: erucic acid).

In this way, starting from readily available technical plant oils dimethyl-1,18-octadecanedioate and the even longer chain dimethyl-1,26-hexacosanedioate were prepared in polymerization grade purity ($\geq$ 99 %). Both compounds after reduction to the corresponding diols, stoichiometrically with $LiAlH_4$ or by catalytic hydrogenation with Saudan's ruthenium catalyst, were used as monomers for the synthesis of linear long-chain polyesters. The obtained materials, namely poly[1,18-octadecanediyl-1,18-octadecanedioate] (**PE-18.18**) and poly[1,26-hexacosanediyl-1,26-hexacosanedioate] (**PE-26.26**) both possess melting points and crystallization temperatures that are significantly higher than for conventional aliphatic polyesters of shorter chain length and already compare with typical thermoplastics. Polyester **PE-26.26** for example features a melting-point of T_m = 114 °C which is unsurpassed among the long-chain all-aliphatic polyesters reported to date.

A different route to long chain α,ω-difunctional compounds and their corresponding polycondensates[2] has recently been found with isomerizing alkoxycarbonylation (**Figure 8.1**). This reaction, first observed by Cole-Hamilton for fatty acid esters[3] 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. In this way odd carbon numbered products with full molecular feedstock incorporation are formed. Starting from technical grade methyl ester of high oleic sunflower oil dimethyl-1,19-nonadecanedioate is obtained in polycondensation grade purity. Likewise, dimethyl-1,23-tricosanedioate is derived from methyl erucate. The successful scale-up now renders both intermediates available on a 100 g scale in > 99 % purity (**Figure 8.2**).

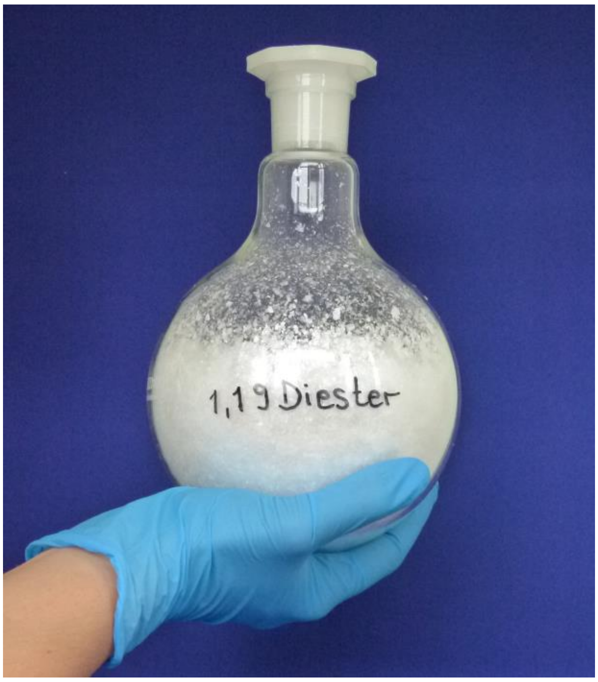


Figure 8.2: Photograph of dimethyl-1,19-nonadecanedioate as obtained from isomerizing alkoxycarbonylation of high oleic sunflower oil.

Polyesters prepared from these long-chain dicarboxylic acids by polycondensation with diols generated from the former by reduction, show high melting points ($T_m > 100$ °C) and crystallization temperatures suitable for thermoplastic processing.[2] An appropriate polycondensation protocol yielded these polymers with number average molecular weights of M_n 3.0×10^4 g mol^{-1} which imparts them with desirable ductile, non-brittle properties. Both, poly[1,19-nonadecadiyl-1,19-nonadecanedioate] (**PE-19.19**) and poly[1,23-tricosadiyl-1,23-tricosanedioate] (**PE-23.23**) as well, possess an elongation at break of > 600 % and a Young's modulus of 400 MPa. Furthermore, first tests on the hydrolytic degradation revealed a good stability in concentrated and diluted acidic and basic aqueous media. In meeting also the demands of injection molding and film extrusion[4] it could be demonstrated that these renewable resource-based polymers offer prospects for novel bio-based packaging films or moldings.

The polyethylene-like crystallinity arising from the long-chain monomers also offers itself to impart elastomeric properties, as demonstrated by novel all-aliphatic thermoplastic polyester elastomers (**Figure 8.3**).

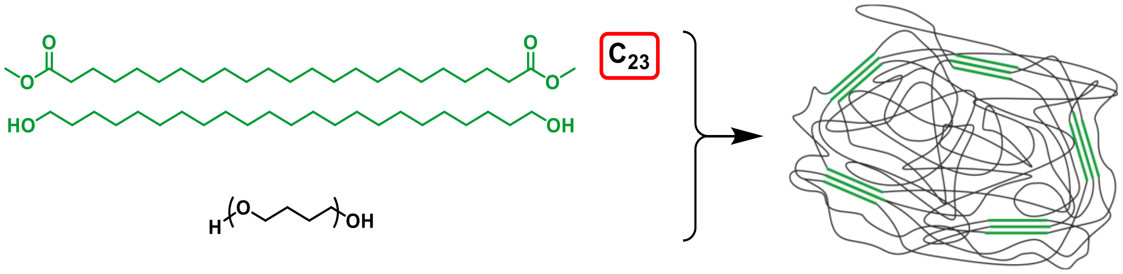
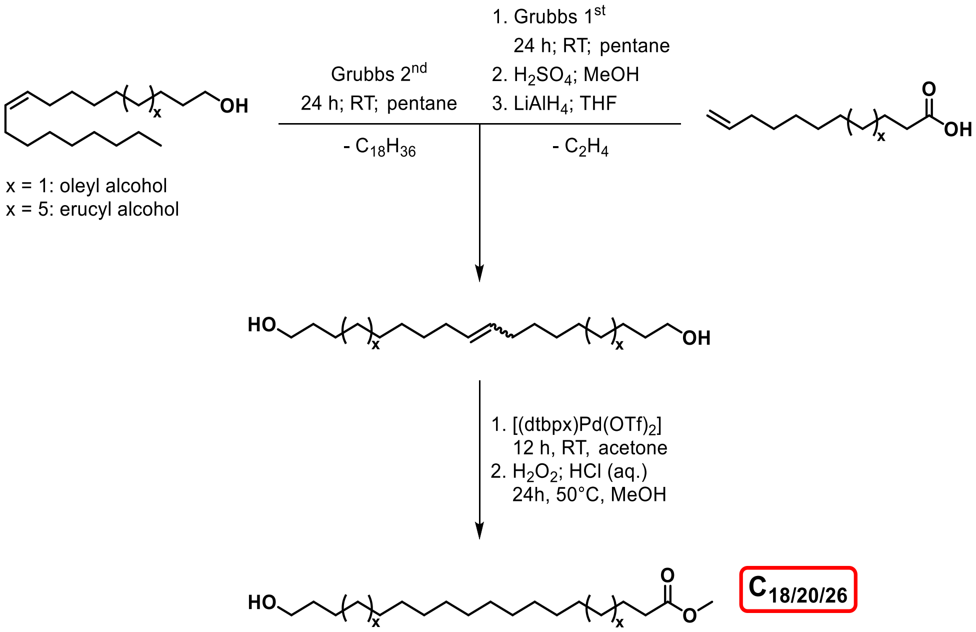


Figure 8.3: Schematic representation of segmented thermoplastic polyester elastomers based on long-chain, aliphatic hard segments.

Polycondensation of dimethyl-1,23-tricosanedioate and 1,23-tricosanediol with diol-terminated poly(tetramethylene glycol), which is also accessible from renewable (carbohydrate) feedstocks, yields polyester-polyether copolymers with molecular weights up to M_n 6×10^4 g mol^{-1}. The long-chain aliphatic segments provide physical crosslinking that imparts elastomeric behavior to these thermoplastic materials. A particularly high recovery was observed at ca. 65 wt.-% (50 mol-% of the total diols employed) of $PTMG_{2000}$ soft segments. Compared to mid-chain analogues based on C_{12} aliphatic monomers, melting points are significantly enhanced. DSC analysis of TPE-$C_{23}PTMG_{1000}$-62wt.-% and TPE-$C_{23}PTMG_{2000}$-65wt.-% revealed melting points of 68 °C and 86 °C, respectively, that is 20 °C higher than for their mid-chain analogues at comparable copolyester mass compositions and chain lengths of the polyether segments. This is practically relevant, as the latter materials based on traditional mid-chain monomers appear prone to a softening and loss of their elastomeric properties upon temperature variations of the ambient conditions.

For A_2+B_2 syntheses of polyesters presented above extremely pure monomers are required in order to achieve any substantial molecular weights. Furthermore upon dosing the long-chain monomers to the reaction mixture an accurate control of the stoichiometric balance between the diol and the diacid (or the diacid derivate) is necessary. This can be circumvented using an AB-type polycondensation approach. However, unsymmetrical α,ω-difunctionalized long-chain monomers are not easily accessible through conventional routes. Here, a redox-isomerization of monounsaturated diols, obtained from self-metathesis of fatty acid derivatives, was found to be viable for the synthesis of linear, long-chain ω-hydroxy aldehydes, which after selective oxidation of the aldehyde functionality can be converted into ω-hydroxy carboxylic acid esters of different chain-length (**Scheme 8.1**). Compared to the aforementioned routes to A_2+B_2 monomers, the procedure at the present point is yet less practicable in that it always required column chromatographic work-up.



Scheme 8.1: Redox isomerization of monounsaturated diols obtained from self-metathesis of fatty acid derivatives.

Polycondensation of the unsymmetrical AB-type monomers prepared according to this protocol afforded long-chain aliphatic polyesters, namely poly[ω-hydroxyl octadecanoic acid] (**PE-18**) and poly[ω-hydroxyl eicosanoic acid] (**PE-20**). Molecular weights as determined by end-group analysis by ^{1}H-NMR spectroscopy, as well as high temperature GPC measurements, revealed number-average molecular weights in the order of several 10^4 g mol^{-1}. Thermal analysis exhibits a melting point of T_m = 101 °C (T_c = 76 °C, ΔH_m = 143 J g^{-1}) for **PE-18**, whereas for the even longer chain aliphatic polyester **PE-20** a melting point of T_m = 103 °C (T_c = 84 °C, ΔH_m = 166 J g^{-1}) was found.

Although all the different approaches discussed so far are promising catalytic routes for the generation of long-chain α,ω-difunctional monomers, they all rely on seed oils. This raises potential issues such as consumption of land and irrigation water, a competition with food production, inefficient yields per time and area, and the associated logistics of harvesting and collection. Considering this background, algae oils are currently receiving much awareness for the generation of higher value chemicals and polymer materials. This, however, requires appropriate chemical conversions and catalysts compatible with algae oil. Thus in an exemplary approach (**Figure 8.5**) mixed linear long-chain polyesters were synthesized from crude lipids of the diatom *Phaeodactylum tricornutum*.

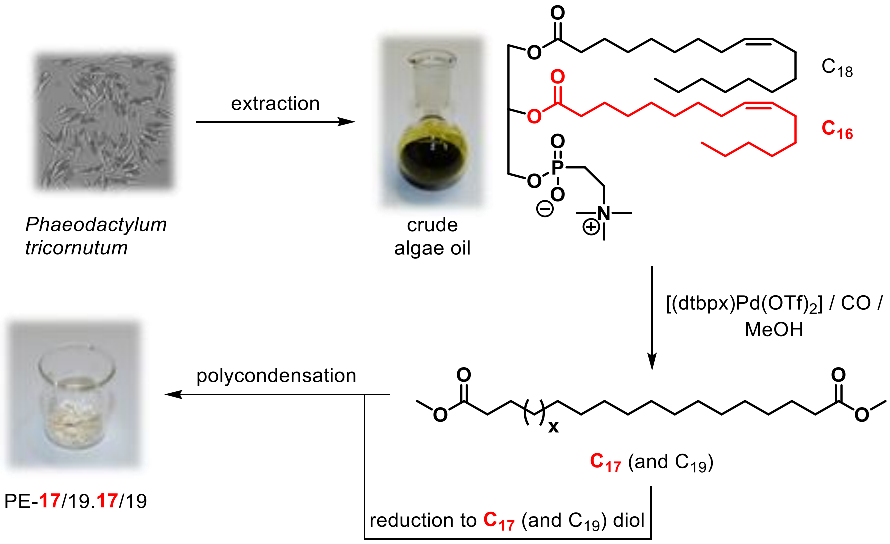


Figure 8.5: Exemplary approach to yield mixed, linear long-chain aliphatic polyester from algae.

Lipid extraction with hydrocarbon solvent, additional acidic hydrolysis to cleave ester functionalities, and ultrasonication to destroy the cells yielded a multicomponent mixture containing amongst others unsaturated fatty acid (16:1, 18:1 and 20:5) phosphocholine triglycerides. Exposure of this crude algae oil to CO and methanol with the known catalyst precursor [1,2-bis{(di-*tert*-butylphosphino)methyl}benzene palladium ditriflate] resulted in isomerization/methoxycarbonylation of the unsaturated fatty acids into a mixture of linear 1,17- and 1,19-diesters in high purity (≥ 99 %). Polycondensation with a mixture of the corresponding diols yielded a novel mixed polyester **PE-17/19.17/19** with an advantageously high melting temperature of T_m = 99 °C as a result of the crystallizable linear segments originating from the algae oil lipids. This melting point is in line with neat model polyesters-X.X (**Figure 7.6**) prepared from the genuine samples for gas chromatographic identification (**PE-17.17**: T_m = 99 °C, **PE-21.21**: T_m = 104 °C and **PE-25.25**: T_m = 108 °C) and reported data for other polyester-X.X with odd numbers of carbon atoms in the repeat units (**PE-19.19**: T_m = 103 °C and **PE-23.23**: T_m = 108 °C).

8.1 References

1. a) High Turnover Numbers with Ruthenium-Based Metathesis Catalysts. Dinger, M. B.; Mol, J. C. *Adv. Synth. Catal.* **2002**, *344*, 671-677. b) Metathesis of Unsaturated Fatty Acids: Synthesis of Long-Chain Unsaturated-α,ω-Dicarboxylic Acids. Ngo, H.; Jones, K.; Foglia, T. *J. Am. Oil Chem. Soc.* **2006**, *83*, 629-634. c) Polyesters by Lipase-Catalyzed Polycondensation of Unsaturated and Epoxidized Long-Chain α,ω-Dicarboxylic Acid Methyl Esters with Diols. Warwel, S.; Demes, C.; Steinke, G. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 1601-1609.
2. a) Linear Semicrystalline Polyesters from Fatty Acids by Complete Feedstock Molecule Utilization. Quinzler, D.; Mecking, S. *Angew. Chem. Int. Ed.* **2010**, *49*, 4306-4308. b) Long-Chain Linear C_{19} and C_{23} Monomers and Polycondensates from Unsaturated Fatty Acid Esters. Stempfle, F.; Quinzler, D.; Heckler, I.; Mecking, S. *Macromolecules* **2011**, *44*, 4159-4166.
3. Dicarboxylic Acid Esters from the Carbonylation of Unsaturated Esters under Mild Conditions, Jiménez-Rodriguez, C.; Eastham, G. R.; Cole-Hamilton, D. J. *Inorg. Chem. Commun.* **2005**, *8*, 878-881.
4. Long-chain aliphatic polyesters from plant oils for injection molding, film extrusion and electrospinning. Stempfle, F.; Ritter, B. S.; Mülhaupt, R.; Mecking, S. *Green Chem.* **2014**, *16*, 2008-2014.

9 Literature

- Almontassir, A.; Gestí, S.; Franco, L.; Puiggalí, J. *Macromolecules* **2004**, *37*, 5300-5309.
- Anderson, D. R.; Ung, T.; Mkrtumyan, G.; Bertrand, G.; Grubbs, R. H.; Schrodi, Y. *Organometallics* **2008**, *27*, 563-566.
- Anneken, D. J.; Both, S.; Christoph, R.; Fieg, G.; Steinberner, U.; Westfechtel, A. in *Ullmann's Encyclopedia of Industrial Chemistry, Vol. 14* (Eds: Gerhartz, W.; Elver, B.), Wiley-VCH, Weinheim, **2000**, pp. 73-116.
- Arriola, D. J.; Carnahan, E. M.; Hustad, P. D.; Kuhlman, R. L.; Wenzel, T. T. *Science* **2006**, *312*, 714-719.
- Arriola, D. J.; Carnahan, E: M:; Cheung, Y. W.; Devore, D. D.; Graf, D. D.; Hustad, P. D.; Kuhlman, R. L.; Li Pi Shan, C.; Poon, B. C.; Roof, G. R.; Stevens, J. C.; Stirn, P. J.; Wenzel, T. T. (Dow Global Technologies), WO 2005/090427 (A2), **2005**.
- Baier, M. C.; Zuideveld, M. A.; Mecking, S. *Angew. Chem. Int. Ed.* **2014**, *53*, 9722-9744.
- Barbiroli, G.; Lorenzetti, C.; Berti, C.; Fiorini, M.; Manaresi, P. *Eur. Polym. J.* **2003**, *39*, 655-661.
- Behr, A.; Obst, D.; Schulte, C.; Schosser, T. *J. Mol. Catal. A: Chem.* **2003**, *206*, 179-184.
- Behr, A.; Obst, D.; Westfechtel, A. *Eur. J. Lipid Sci. Technol.* **2005**, *107*, 213-219.
- Bergbreiter, D. E.; Whitesides, G. M. *J. Org. Chem.* **1975**, *40*, 779-782.
- Bidd, I.; Holdup, D. W.; Whiting, M. C. *J. Chem. Soc., Perkin Trans. 1* **1987**, 2455-2463.
- Biermann, U.; Bornscheuer, U.; Meier, M. A. R.; Metzger, J. O.; Schäfer, H. J. *Angew. Chem. Int. Ed.* **2011**, *50*, 3854-3871.
- Blomquist, A. T.; Johnson, J. R.; Diuguid, L. I.; Shillington, J. K.; Spencer, R. D. *J. Am. Chem. Soc.* **1952**, *74*, 4203-4204.
- Bouyahyi, M.; Pepels, M. P. F.; Heise, A.; Duchateau, R. *Macromolecules* **2012**, *45*, 3356-3366
- Bowler, C.; Allen, A. E.; Badger, J. H.; Grimwood, J.; Jabbari, K.; Kuo, A.; Maheswari, U.; Martens, C.; Maumus, F.; Otillar, R. P.; Rayko, E.; Salamov, A.; Vandepoele, K.; Beszteri, B.; Gruber, A.; Heijde, M.; Katinka, M.; Mock, T.; Valentin, K.; Verret, F.; Berges, J. A.; Brownlee, C.; Cadoret, J.-P.; Chiovitti, A.; Choi, C. J.; Coesel, S.; De Martino, A.; Detter, J. C.; Durkin, C.; Falciatore, A.; Fournet, J.; Haruta, M.; Huysman, M. J. J.; Jenkins, B. D.; Jiroutova, K.; Jorgensen, R. E.; Joubert, Y.; Kaplan, A.; Kroger, N.; Kroth, P. G.; La Roche, J.; Lindquist, E.; Lommer, M.; Martin-Jezequel, V.; Lopez, P. J.; Lucas, S.; Mangogna, M.; McGinnis, K.; Medlin, L. K.; Montsant, A.; Secq, M.-P. O.-L.; Napoli, C.; Obornik, M.; Parker, M. S.; Petit, J.-L.; Porcel, B. M.; Poulsen, N.; Robison, M.; Rychlewski, L.; Rynearson, T. A.; Schmutz, J.; Shapiro, H.; Siaut, M.; Stanley, M.; Sussman, M. R.; Taylor, A.

R.; Vardi, A.; von Dassow, P.; Vyverman, W.; Willis, A.; Wyrwicz, L. S.; Rokhsar, D. S.; Weissenbach, J.; Armbrust, E. V.; Green, B. R.; van de Peer, Y.; Grigoriev, I. V. *Nature* **2008**, *456*, 239-244.

- Brand, T.; Brenner, G.; Franzmann, G.; Zagefka, H.-D. (Degussa AG), WO 2005/090428 A1 (**2005**).
- Brehmer, B. In *Bio-Based Plastics: Materials and Applications*, Kabasci, S., Ed.; Wiley: Chichester, **2004**, 275-294.
- Brenner, G.; Koschabek, R. (Evonik Degussa GmbH), WO 2009/010324 A2 (**2009**).
- Brooke, G. M.; Burnett, S.; Mohammed, S.; Proctor, D.; Whiting, M. C. *J. Chem. Soc., Perkin Trans. 1* **1996**, 1635-1645.
- Brown, A. C.; Walker, J. *J. Liebigs Ann. Chem.* **1891**, *261*, 107-128.
- Brown, M.; Witsiepe, W. K., *Rubber Age* **1972**, *104*, 35-42.
- Buchta, E.; Huhn, C. *J. Liebigs Ann. Chem.* **1966**, *695*, 42-48.
- Bunn, C. W. *J. Polym. Sci.* **1955**, *16*, 323-343.
- Burdett, K. A.; Harris, L. D.; Margl, P.; Maughon, B. R.; Mokhtar-Zadeh, T.; Saucier, P. C.; Wasserman, E. P. *Organometallics* **2004**, *23*, 2027-2047.
- Cai, J.; Hsiao, B. S.; Gross, R. A. *Macromolecules* **2011**, *44*, 3874-3883.
- Cai, J.; Liu, C.; Cai, M.; Zhu, J.; Zuo, F.; Hsiao, B. S.; Gross, R. A. *Polymer* **2010**, *51*, 1088-1099.
- Cao, Z.; Gao, H.; Liu, M.; Jiao, P. *Biotechnol. J.* **2006**, *1*, 68-74.
- Carothers, W. H. In *Collected Papers of Wallace Hume Carothers on High Polymeric Substances*, Mark, H.; Whitby, G. S., Eds.; Interscience Publishers: New York, **1940**.
- Carothers, W. H. *Trans. Faraday Soc.* **1936**, *32*, 39-49.
- Carothers, W. H.; Arvin, J. A. *J. Am. Chem. Soc.* **1929**, *51*, 2560-2570.
- Ceccorulli, G.; Scandola, M.; Kumar, A.; Kalra, B.; Gross, R. A. *Biomacromolecules* **2005**, *6*, 902-907.
- Cella, R. J., J. *Polym. Sci: Polym. Symp.* **1973**, *42*, 727-740.
- Chatterjee, A. K.; Choi, T.-L.; Sanders, D. P.; Grubbs, R. H. *J. Am. Chem. Soc.* **2003**, *125*, 11360-11370.
- Chatterjee, D. P.; Mandal, B. M., *Macromol. Symp.* **2006**, *240*, 224-231.
- Chikkali, S.; Mecking, S. *Angew. Chem. Int. Ed.* **2012**, *51*, 5802-5808.
- Chisti, Y. *Biotechnol. Adv.* **2007**, *25*, 294-306.
- Cho, I.; Lee, K.; *Macromol. Chem. Phys.* **1997**, *198*, 861-869.
- Choi, K. C.; Lee, E. K.; Choi, S. Y. *J. Ind. and Eng. Chem.* **2003**, *9*, 518-525.

- Christl, J. T.; Roesle, P.; Stempfle, F.; Müller, G.; Caporaso, L.; Cavallo, L.; Mecking, S. *ChemSusChem* **2014**, *7*, 3491-3495.
- Christl, J. T.; Roesle, P.; Stempfle, F.; Wucher, P.; Göttker-Schnetmann, I.; Müller, G.; Mecking, S. *Chem. Eur. J.* **2013**, *19*, 17131-17140.
- Chuit, P. *Helv. Chim. Acta* **1926**, *9*, 264-278.
- Chuit, P.; Hausser, J. *Helv. Chim. Acta* **1929**, *12*, 850-859.
- Cohen, S. A.; Luetkens, M. L.; Balakrishnan, C.; Snyder, R. (Elevance Renewable Sciences), WO 2011/046872 A2 (**2011**).
- Cole-Hamilton, D. J. *Angew. Chem. Int. Ed.* **2010**, *49*, 8564-8568.
- Colquhoun, H. M.; Holton, J.; Thompson, D. J.; Twigg, M. V. in *New Pathways for Organic Synthesis*, Eds. Colquhoun, H. M.; Holton, J.; Thompson, D. J.; Twigg, M. V. Plenum Press: New York, **1984**; pp 173-193.
- Corma, A.; Iborra, S.; Velty, A. *Chem. Rev.* **2007**, *107*, 2411-2502.
- De Geus, M.; van der Meulen, I.; Goderis, B.; van Hecke, K.; Dorschu, M.; van der Werff, H.; Koning, C. E.; Heise, A. *Polym. Chem.* **2010**, *1*, 525-533.
- De Ten Hove, C. L. F.; Penelle, J.; Ivanov, D. A.; Jonas, A. M. *Nat. Mater.* **2004**, *3*, 33-37.
- Dinger, M. B.; Mol, J. C. *Adv. Synth. Catal.* **2002**, *344*, 671-677.
- Dinger, M. B.; Mol, J. C. *Organometallics* **2003**, *22*, 1089-1095
- Dinger, M. B.; Mol, J. C. *Eur. J. Inorg. Chem.* **2003**, *15*, 2827-2833.
- Djigoué, G. B.; Meier, M. A. R. *Appl. Catal. A* **2009**, *368*, 158-162.
- Eschenfeldt, W. H.; Zhang, Y.; Samaha, H.; Stols, L.; Eirich, L. D.; Wilson, C. R.; Donnelly, M. I. *Appl. Environ. Microbiol.* **2003**, *69*, 5992-5999.
- Evans, R. D.; Mighton, H. R.; Flory, P. J. *J. Am. Chem. Soc.* **1950**, *72*, 2018-2028.
- Fairweather, D. A. *Proc. R. Soc. Edinburgh* **1925**, *45*, 283-285.
- Fairweather, D. A. *Proc. R. Soc. Edinburgh* **1926**, *46*, 71-75.
- Fakirov, S., *Transreactions in condensation polymers*. Wiley-VCH: Weinheim; New York, **1999**.
- Firdaus, M.; Montero de Espinosa, L.; Meier, M. A. R. *Macromolecules* **2011**, *44*, 7253-7262.
- Folch, J.; Lees, M.; Stanley, G. H. S. *J. Biol. Chem.* **1957**, *226*, 497-509.
- Foley, P. M.; Beach, E. S.; Zimmerman, J. B. *Green Chem.* **2011**, *13*, 1399-1405.
- Form S1 SEC filing by Elevance Renewable Sciences of September 20, 2011 (IPO registration).
- Forman, G. S.; Bellabarba, R. M.; Tooze, R. P.; Slawin, A. M. Z.; Karch, R.; Winde, R. *J. Organomet. Chem.* **2006**, *691*, 5513-5516.

- Forman, G. S.; McConnell, A. E.; Hanton, M. J.; Slawin, A. M. Z.; Tooze, R. P.; van Rensburg, W. J.; Meyer, W. H.; Dwyer, C.; Kirk, M. M.; Serfontein, D. W. *Organometallics* **2004**, *23*, 4824-4827.
- Frank, N. J.; Shou-Kuan, F.; Jun, H.; Xiaoying, Y. (Eastern Michigan University), U.S. Patent 5,641,854 (**1997**).
- Fu, H.; Kulshrestha, A. S.; Gao, W.; Gross, R. A.; Baiardo, M.; Scandola, M. *Macromolecules* **2003**, *36*, 9804-9808.
- Fujisawa, T.; Sato, T.; Kawara, T.; Tago, H. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 345-346.
- Fuller, C. S.; Frosch, C. J., J. Am. Chem. Soc. 1939, 61, 2575-2580.
- Furst, M. R. L.; Le Goff, R.; Quinzler, D.; Mecking, S.; Botting, C. H.; Cole-Hamilton, D. J. *Green Chem.* **2012**, *14,* 472-477.
- Furst, M. R. L.; Seidensticker, T.; Cole-Hamilton, D. J. *Green Chem.* **2013**, *15*, 1218-1225.
- Ganske, F.; Meyer, H. H.; Deutz, H.; Bornscheuer, U. *Eur. J. Lipid Sci. Tech.* **2003**, *105*, 627-632.
- Geider, R. J.; Delucia, E. H.; Falkowski, P. G.; Finzi, A. C.; Grime, J. P.; Grace, J.; Kana, T. M.; La Roche, J.; Long, S. P.; Osborne, B. A.; Platt, T.; Prentice, I. C.; Raven, J. A.; Schlesinger, W. H.; Smetacek, V.; Stuart, V.; Sathyendranath, S.; Thomas, R. B.; Vogelmann, T. C.; Williams, P.; Woodward, F. I. *Glob. Change Biol.* **2001**, *7*, 849-882.
- Genas, M. *Angew. Chem.* **1962**, *74*, 535-540.
- Gestí, S.; Casas, M. T.; Puiggali, J. *Eur. Polym. J.* **2008**, *44*, 2295-2307.
- Ghebreyessus, K. Y.; Angelici, R. J. *Organometallics* **2006**, *25*, 3040-3044.
- Gimeno, N.; Formentín, P.; Steinke, J. H. G.; Vilar, R. *Eur. J. Org. Chem.* **2007**, *2007*, 918-924.
- Goebel, C. G.; Brown, A. C.; Oehlschlaeger, H. F.; Rolfes, R. P. (Emery Industries), U.S. Patent 2,813,113 A (**1957**).
- Grieveson, B. M. *Polymer* **1960**, *1*, 499-512.
- Gross, R. A., Lu, W., Ness, J., Minshull, J. (Polytechnic Institute of New York University), WO 2011/008232 (**2011**).
- Grotjahn, D. B.; Larsen, C. R.; Gustafson, J. L.; Nair, R.; Sharma, A. *J. Am. Chem. Soc.* **2007**, *129*, 9592-9593.
- Grubbs, R. H. *Handbook of Metathesis, Vol. 1-3*; Wiley-VCH: Weinheim, **2003**.
- Guillard, R. L. in *Culture of Marine Invertebrate Animals*, (Eds Smith, W. L.; Chanley, M. H.), Springer US, **1975**, pp. 29-60.
- Guillard, R. R. L.; Ryther, J. H. Can. *J. Microbiol.* **1962**, *8*, 229-239.

- Günthard, H. H.; Heinemann, S. D.; Prelog, V. *Helv. Chim. Acta* **1953**, *36*, 1147-1159.
- Guschina, I. A.; Harwood, J. L. *Progr. Lipid Res.* **2006**, *45*, 160-186.
- Heidbreder, A.; Höfer, R.; Grützmacher, R.; Westfechtel, A.; Blewett, C. W. *Fett/Lipid* **1999**, *101*, 418-424.
- Hellmann, F.; Verburg, P. H. *J. Environ. Manage.* **2010**, *91*, 1389-1396.
- Hiemenz, P. C.; Lodge, T. P. *Polymer Chemistry, 2nd ed.*; CRC Press: Boca Raton, FL, **2007**.
- Hill, K. *Pure Appl. Chem.* **2000**, *72*, 1255-1264.
- Hoeschele, G. K.; Witsiepe, W. K., *Angew. Makromol. Chem.* **1973**, *29*, 267-289
- Holden, G.; Bishop, E. T.; Legge, N. R., *J. Polym. Sci. Part C: Polym. Symp.* **1969**, *26*, 37-57.
- Holden, G.; Kricheldorf, H. R.; Quirk, R. P., *Thermoplastic Elastomers.* Hanser: Munich, **2004**.
- Hong, S. H.; Day, M. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **2004**, *126*, 7414-7415.
- Hong, S. H.; Sanders, D. P.; Lee, C. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **2005**, *127*, 17160-17161.
- Huber, T.; Firlbeck, D.; Riepl, H. M. *J. Organomet. Chem.* **2013**, *744*, 144-148.
- Huf, S.; Krügener, S.; Hirth, T.; Rupp, S.; Zibek, S. *Eur. J. Lipid Sci. Technol.* **2011**, *113*, 548-561.
- Hünig, S.; Buysch, H.-J. *Chem. Ber.* **1967**, *100*, 4010-4016.
- Hünig, S.; Lendle, W. *Chem. Ber.* **1960**, *93*, 913-920.
- Hünig, S.; Lücke, E.; Brenninger, W. *Organic Syntheses*, Coll. Vol. 5, p.533 (**1973**); Vol. 43, p.34 (**1963**).
- Hünig. S.; Lücke, E. *Chem. Ber.* **1959**, *92*, 652-662.
- Inci, B.; Wagener, K. B. *J. Am. Chem. Soc.* **2011**, *133*, 11872-11875.
- Inherent^{TM} C_{18} diacid. Beuhler, A. *Bioplastics Magazine* **2013**, *8*, 8-10.
- Iranpoor, N.; Mottaghinejad, E. *J. Organomet. Chem.* **1992**, *423*, 399-404.
- Ishioka, R.; Kitakuni, E.; Ichikawa; Y. In *Biopolymers*; Steinbüchel, A.; Doi, Y. (Eds.); Wiley-VCH: Weinheim, **2002**; Vol. 4, 275-297
- Ito, M.; Kubo, M.; Tsuruta, A.; Tanaka, K. *J. Polym. Sci.: Polym. Phys. Ed.*, **1978**, *16*, 1435-1446.
- Jiménez-Rodriguez, C.; Eastham, G. R.; Cole-Hamilton, D. J. *Inorg. Chem. Commun.* **2005**, *8*, 878-881.
- Jiménez-Rodriguez, C.; Foster, D. F.; Eastham, G. R.; Cole-Hamilton, D. J. *Chem. Commun.* **2004**, 1720-1721.
- Jose, J.; Pourfallah, G.; Leao, A. L.; Narine, S. S. *Polym. Int.* **2014**, *63*, 1902-1911.
- Jose, J.; Pourfallah, G.; Merkley, D.; Li, S.; Bouzidi, L.; Leao, A. L.; Narine, S. S. *Poly. Chem.* **2014**, *5*, 3203-3213.

- Kanamoto, T.; Tanaka, K.; Nagai, H. *J. Polym. Sci., Part A-2: Polym. Phys.* **1971**, *9*, 2043-2060.
- Kerton, F. M.; Liu, Y.; Omari, K. W.; Hawboldt, K. *Green Chem.* **2013**, *15*, 860-871.
- Kolattukudy, P. E. *Science* **1980**, *208*, 990-1000.
- Köpnick, H.; Schmidt, M.; Brügging, W.; Rüter, J.; Kaminsky, W., In *Ullmann's Encyclopedia of Industrial Chemistry*, Gerhartz, W.; Elvers, B. (Eds.) Wiley-VCH: Weinheim, **2000**.
- Körner, H. J.; Deerberg, G. *Chem. Ing. Tech.* **2009**, *81*, 1823-1828.
- Korshak, V. V.; Vinogradova, S. V. *Polyesters*; Pergamon Press: Oxford, U.K., **1965**.
- Korshak, V. V.; Vinogradova, S. V.; Vlasova, E. S. *Russ. Chem. Bull.* **1954**, *3*, 949-955.
- Korshak, W. V.; Vinogradova, S. V. *Russ. Chem. Bull.* **1953**, *2*, 995-998.
- Kreuchunas, A. *J. Am. Chem. Soc.* **1953**, *75*, 3339-3344.
- Kroha, K. *Inform.* **2004**, *15*, 568-571.
- Kroth, P. in *Protein Targeting Protocols, Vol. 390* (Ed: Giezen, M.), Humana Press, **2007**, pp. 257-267.
- Kuźnik, N.; Krompiec, S. *Coord. Chem. Rev.* **2007**, *251*, 222-233.
- Le Fevere de Ten Hove, C. PhD thesis, Université catholique de Louvain, Louvain-la-Neuve (**2001**).
- Le Fevere de Ten Hove, C.; Penelle, J.; Ivanov, D. A.; Jonas, A. M., *Nat. Mater.* **2004**, *3*, 33-37.
- Lehman Jr, S. E.; Schwendeman, J. E.; O'Donnell, P. M.; Wagener, K. B. *Inorg. Chim. Acta* **2003**, *345*, 190-198.
- Lehman, S. E.; Wagener, K. B. *Macromolecules* **2001**, *35*, 48-53.
- Lemke, D. W.; Uptain, K. D.; Amore, F.; Abraham, T. (Elevance Renewable Sciences), WO 2009/020667 A1, **2009**.
- Letizia Focarete, M.; Scandola, M.; Kumar, A.; Gross, R. A., *J. Polym. Sci., Part B: Polym. Phys.* **2001**, *39*, 1721-1729.
- Lettré, H.; Jahn, A. *Chem. Ber.* **1952**, *85*, 346-351.
- Levitan, O.; Dinamarca, J.; Hochman, G.; Falkowski, P. G. *Trends Biotechnol.* **2014***,* *32*, 117-124.
- Liu, C.; Liu, F.; Cai, J.; Xie, W.; Long, T. E.; Turner, S. R.; Lyons, A.; Gross, R. A. *Biomacromolecules* **2011**, *12*, 3291-3298.
- Lu, W.; Ness, J. E.; Xie, W.; Zhang, X.; Minshull, J.; Gross, R. A. *J. Am. Chem. Soc.* **2010**, *132*, 15451-15455.
- Maglio, G.; Marchetta, C.; Botta, A.; Palumbo, R.; Pracella, M. *Eur. Polym. J.* **1979**, *15*, 695-699.

- Mandelkern, L.; Alamo, R. G. in *Physical Properties of Polymers Handbook*; Ed. Mark, J. E.; Springer: New York, **2007**; pp 165-186.
- Marinescu, S. C.; Schrock, R. R.; Muller, P.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2009**, *131*, 10840-10841.
- Martello, M. T.; Hillmyer, M. A. *Macromolecules* **2011**, *44*, 8537-8545.
- Marx, V. M.; Sullivan, A. H.; Melaimi, M.; Virgil, S. C.; Keitz, B. K.; Weinberger, D. S.; Bertrand, G.; Grubbs, R. H. *Angew. Chem. Int. Ed.* **2015**, *54*, 1919-1923.
- Mascarelli, A. L. *Nature* **2009**, *461*, 460-461.
- Mata, T. M.; Martins, A. A.; Caetano, N. S. *Renew. Sust. Energ. Rev.* **2010**, *14*, 217-232.
- Mecking, S.; Quinzler, D.; WO 2011/089256 A1 (**2011**).
- Meier, M. A. R. *Macromol. Chem. Phys.* **2009**, *210*, 1073-1079.
- Menges, M. G.; Penelle, J.; Le Fevere de Ten Hove, C.; Jonas, A. M.; Schmidt-Rohr, K. *Macromolecules* **2007**, *40*, 8714-8725.
- Meyer, W. H.; McConnell, A. E.; Forman, G. S.; Dwyer, C. L.; Kirk, M. M.; Ngidi, E. L.; Blignaut, A.; Saku, D.; Slawin, A. M. Z. *Inorg. Chim. Acta* **2006**, *359*, 2910-2917.
- Mikolajczak, K. L.; Miwa, T. K.; Earle, F. R.; Wolff, I. A.; Jones, Q. *J. Am. Oil. Chem. Soc.* **1961**, *38*, 678-681.
- Mol, J. C. *Green Chem.* **2002**, *4*, 5-13.
- Mol, J. C. *J. Mol. Catal.* **1994**, *90*, 185-199.
- Mol. J. C. *Top. Catal.* **2004**, *27*, 97-104.
- Morton, M.; McGrath, J. E.; Juliano, P. C., *J. Polym. Sci. Part C: Polym. Symp.* **1969**, *26*, 99-115.
- Mosnáček, J.; Yoon, J. A.; Juhari, A.; Koynov, K.; Matyjaszewski, K., *Polymer* **2009**, 50, 2087-2094.
- Mutlu, H.; Hofsa; Montenegro, R. E.; Meier, M. A. R. *RSC Advances* **2013**, *3*, 4927-4934.
- Naughton, F. C. *J. Am. Oil Chem. Soc.* **1974**, *51*, 65-71.
- Ngo, H. L.; Foglia, T. A. *J. Am. Oil Chem. Soc.* **2007**, *84*, 777-784.
- Ngo, H. L.; Jones, K.; Foglia, T. A. *J. Am. Oil Chem. Soc.* **2006**, *83*, 629-634.
- Ngo, H.; Foglia, T. A. (United States Department of Agriculture) U.S. Patent 7,534,917 (B1), **2009**.
- Ngo, H.; Jones, K.; Foglia, T. *J. Am. Oil Chem. Soc.* **2006**, *83*, 629-634.
- Nivinskiene, O.; Butkiene, R.; Mockute, D. Chemija **2003**, *14*, 52-56.
- Ortmann, P.; Heckler, I.; Mecking, S. *Green Chem.* **2014**, *16*, 1816-1827.
- Ortmann, P.; Mecking, S. *Macromolecules* **2013**, *46*, 7213-7218.

- Ouhadi, T.; Abdou-Sabet, S.; Wussow, H.-G.; Ryan, L. M.; Plummer, L.; Baumann, F. E.; Lohmar, J.; Vermeire, H. F.; Malet, F. L. G., Thermoplastic Elastomers. in *Ullmann's Encyclopedia of Industrial Chemistry*, *Vol. 14* (Eds: Gerhartz, W.; Elver, B.), Wiley-VCH: Weinheim, **2000**, pp. 1-40.
- Patel, J.; Elaridi, J.; Jackson, W. R.; Robinson, A. J.; Serelis, A. K.; Such, C. *Chem. Commun.* **2005**, 5546-5547.
- Patel, J.; Mujcinovic, S.; Jackson, W. R.; Robinson, A. J.; Serelis, A. K.; Such, C. *Green Chem.* **2006**, *8*, 450-454.
- Patil, V.; Källqvist, T.; Olsen, E.; Vogt, G.; Gislerød, H. *Aquacult Int.* **2007**, *15*, 1-9.
- Patwardhan, S. A. *Org. Prep. Proced. Int.* **1994,** *26*, 645-670.
- Penelle, J.; Le Fevere de Ten Hove, C.; Schall, J.; Jonas, A.; Hu, W.; Schmidt-Rohr, K.; Waddon, A. J. *Polym. Prepr.* **1999**, *40*, 617-618.
- Pepels, M. P. F.; Hansen, M. R.; Goossens, H.; Duchateau, R., *Macromolecules* **2013**, *46*, 7668-7677.
- Petrović, Z. S. *Polym. Rev.* **2008**, *48*, 109-155.
- Picataggio, S., Deanda, K., Eirich, L. D. (Henkel Research Corp.) WO 1991/06660 (**1991**).
- Picataggio, S.; Deanda, K.; Mielenz, J. *Mol. Cell. Biol.* **1991**, *11*, 4333-4339.
- Picataggio, S.; Rohrer, T.; Deanda, K.; Lanning, D.; Reynolds, R.; Mielenz, J.; Eirich, L. D. *Nat. Biotech.* **1992**, *10*, 894-898.
- Prakash, J. R. *J. Rheol.,* **2002**, *46*, 1353-1380.
- Press release by BASF of March 5, 2015.
- Press release by Elevance Renewable Sciences of February 5, 2014.
- Press release by Elevance Renewable Sciences of July 18, 2013.
- Press release by Elevance Renewable Sciences of October 22, 2013
- Press release by Elevance Renewable Sciences of September 17, 2013.
- Press release by Wilmar International of July 18, 2013.
- Pugh, R. I.; Drent, E.; Pringle, P. G. *Chem. Commun.* **2001**, 1476-1477.
- Quinzler, D.; Mecking, S. *Angew. Chem. Int. Ed.* **2010**, *49*, 4306-4308.
- Quinzler, D.; Mecking, S. *Chem. Commun.* **2009**, *36*, 5400-5402.
- R. Goss, C. Wilhelm, in *Lipids in Photosynthesis, Vol. 30* (Eds: H. Wada, N. Murata), Springer Netherlands, **2010**, pp. 117-137.
- Reis, A.; Rudnitskaya, A.; Blackburn, G. J.; Fauzi, N. M.; Pitt, A. R.; Spickett, C. M. *J. Lipid Res.* **2013**, *54*, 1812-1824.

- Rickert, S. E.; Baer, E.; Wittmann, J. C.; Kovacs, A. J. *J. Polym. Sci., Polym. Phy. Ed.* **1978**, *16*, 895-906.
- Riepl, H. M.; Pettrak, J.; Faulstich, M.; Herrmann, W. A. *Macromol. Symp.* **2010**, *293*, 39-42.
- Roesle, P.; Caporaso, L.; Schnitte, M.; Goldbach, V.; Cavallo, L.; Mecking, S. *J. Am. Chem. Soc.* **2014**, *136*, 16871-16881.
- Roesle, P.; Dürr, C. J.; Möller, H. M.; Cavallo, L.; Caporaso, L.; Mecking, S. *J. Am. Chem. Soc.* **2012**, *134*, 17696-17703.
- Rogers, M. E.; Long, T. E. *Synthetic methods in step-growth polymers*. Wiley-Interscience: Hoboken, N.J., **2003**.
- Rusanova, E. E.; Sebyakin, Y. L.; Volkova, L. V.;. Evstigneeva, R. P. *J. Org. Chem. USSR* **1984**, *20*, 248-251.
- Rybak, A.; Fokou, P. A.; Meier, M. A. R. *Eur. J. Lipid Sci. Technol.* **2008**, *110*, 797-804.
- Saudan, L. A.; Saudan, C. M.; Debieux, C.; Wyss, P. *Angew. Chem. Int. Ed.* **2007**, *46*, 7473-7476.
- Saudan, L.; Dupau, P.; Riedhauser, J.-J.; Wyss, P.; U.S. Patent 7,763,758 (B2), **2010**.
- Schäfer, H.-J. In *Electrochemistry IV*, Steckhan, E., Ed.; Springer: Berlin Heidelberg: **1990**; *Vol. 152*, 91-151.
- Schaffer, S.; Haas, T. *Org. Process Res. Dev.* **2014**, *18*, 752-766.
- Schill, G.; Merkel, C. *Chem. Ber.* **1978**, *111*, 1446-1452.
- Schindler, J.; Meussdoerffer, F.; Giesel-Bühler, H. *Forum Mikrobiologie* **1990**, *13*, 274-281.
- Schlagermann, P.; Göttlicher, G.; Dillschneider, R.; Rosello-Sastre, R.; Posten, C. *J. Combust.* **2012**, *2012*, 1-14.
- Schmidt, A.; Veeman, W. S.; Litvinov, V. M.; Gabriëlse, W., *Macromolecules* **1998**, *31*, 1652-1660.
- Schmidt, B. *Eur. J. Org. Chem.* **2004**, *9*, 1865-1880.
- Schmidt, B. *J. Mol. Catal. A: Chem.* **2006**, *254*, 53-57.
- Schörken, U.; Kempers, P. *Eur. J. Lipid Sci. Technol.* **2009**, *111*, 627-645.
- Schrodi, Y.; Pederson, R. L.; Kaido, H.; Tupy, M. J. (Materia Inc.), WO 2008/046106 A2 (**2008**).
- Schrodi, Y.; Ung, T.; Vargas, A.; Mkrtumyan, G.; Lee, C. W.; Champagne, T. M.; Pederson, R. L.; Hong, S. H. *Clean* **2008**, *36*, 669-673.
- Shalaby, W.; Damiolkowski, D. (Ethicon, Inc.), U.S. Patent 4,140,678 (**1979**).
- Shin, J.; Lee, Y.; Tolman, W. B.; Hillmyer, M. A., *Biomacromolecules* **2012**, *13*, 3833-3840.

- Silvestre, A. J. D.; Neto, C. P.; Gandini, A. In *Monomers, Polymers and Composites from Renewable Resources*, Gandini, M. N. B., Ed.; Elsevier: Amsterdam, **2008**; 305-320.
- Sousa, A. F.; Silvestre, A. J. D.; Gandini, A.; Neto, C. P. *High Perform. Polym.* **2012**, *24*, 4-8.
- Speier, J. L.; Webster, J. A.; Barnes, G. H. *J. Am. Chem. Soc.* **1957**, *79*, 974-979.
- Speier, J. L.; Zimmerman, R.; Webster, J. *J. Am. Chem. Soc.* **1956**, *78*, 2278-2281.
- Stempfle, F.; Ortmann, P.; Mecking, S. *Macromol. Rapid Commun.* **2013**, *34*, 47-50.
- Stempfle, F.; Quinzler, D.; Heckler, I.; Mecking, S. *Macromolecules* **2011**, *44*, 4159-4166.
- Stempfle, F.; Ritter, B. S.; Mülhaupt, R.; Mecking, S. *Green Chem.* **2014**, *16*, 2008-2014.
- Stempfle, F.; Roesle, P.; Mecking, S. In *ACS Symp. Ser.: Biobased Monomers, Polymers and Materials* (Eds.: Richard A. Gross, Patrick B. Smith), **2012**, *1105*, 151-164.
- Stempfle, F.; Schemmer, B.; Oechsle, A.-L.; Mecking, S. *Polym. Chem.* **2015**, *6*, 7133-7137.
- Takeda, T.; Watanabe, H.; Kitahara, T. *Synlett* **1997**, *10*, 1149-1150.
- Thomas, R. M.; Keitz, B. K.; Champagne, T. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **2011**, *133*, 7490-7496.
- Thurier, C.; Fischmeister, C.; Bruneau, C.; Olivier-Bourbigou, H.; Dixneuf, P. H. *ChemSusChem* **2008**, *1*, 118-122.
- Tonon, T.; Harvey, D.; Larson, T. R.; Graham, I. A. *Phytochemistry* **2002**, *61*, 15-24.
- Travert-Branger, N.; Dubois, F.; Carion, O.; Carrot, G.; Mahler, B.; Dubertret, B.; Doris, E.; Mioskowski, C. *Langmuir* **2008**, *24*, 3016-3019.
- Trentacoste, E.; Martinez, A.; Zenk, T. *Photosynth. Res.* **2014**, 1-11.
- Trnka, T. M.; Grubbs, R. H. *Acc. Chem. Res.* **2000**, *34*, 18-29.
- Trost, B. M. *Acc. Chem. Res.* **2002**, *35*, 695-705.
- Trzaskowski, J.; Quinzler, D.; Bährle, C.; Mecking, S. *Macromol. Rapid Commun.* **2011**, *32*, 1352-1356.
- Türünç, O.; Montero de Espinosa, L.; Meier, M. A. R. *Macromol. Rapid Comm.* **2011**, *32*, 1357-1361.
- Ulman, M.; Grubbs, R. H. *J. Org. Chem.* **1999**, *64*, 7202-7207.
- Uma, R.; Crévisy, C.; Grée, R. *Chem. Rev.* **2002**, *103*, 27-52.
- Van Dam, P. B.; Mittelmeijer, M. C.; Boelhouwer, C. *J. Chem. Soc., Chem. Commun.* **1972**, *22*, 1221-1222.
- Van Dam, P.; Mittelmeijer, M.; Boelhouwer, C. *J. Am. Oil Chem. Soc.* **1974**, *51*, 389-392.
- Van der Meulen, I.; de Geus, M.; Antheunis, H.; Deumens, R.; Joosten, E. A. J.; Koning, C. E.; Heise, A. *Biomacromolecules* **2008**, *9*, 3404-3410.

- Van der Meulen, I.; Gubbels, E.; Huijser, S.; Sablong, R. l.; Koning, C. E.; Heise, A.; Duchateau, R. *Macromolecules* **2011**, *44*, 4301-4305.
- Verhé, R. G. In *Renewable Bioresources: Scope and Modification for Non-Food Applications*, Stevens, C. V.; Verhé, R. G., Eds.; Wiley: Chichester: **2004**, 208-250.
- Verkuijlen, E.; Boelhouwer, C. *Fette, Seifen, Anstrichmittel* **1976**, *78*, 444-447.
- Verkuijlen, E.; Kapteijn, F.; Mol, J. C.; Boelhouwer, C. *J. Chem. Soc., Chem. Commun.* **1977**, *7*, 198-199.
- Vilela, C.; Silvestre, A. J. D.; Meier, M. A. R. *Macromol. Chem. Phys.* **2012**, *213*, 2220-2227.
- Vougioukalakis, G. C.; Grubbs, R. H. *Chem. Rev.* **2010**, *110*, 1746-1787.
- Wakselman, M. C. *C. R. Hebd. Seances Acad. Sci.* **1964**, *260*, 5056-5058.
- Walther, G.; Deutsch, J.; Martin, A.; Baumann, F.-E.; Fridag, D.; Franke, R.; Köckritz, A. *ChemSusChem* **2011**, *4* , 1052-1054.
- Wanamaker, C. L.; O'Leary, L. E.; Lynd, N. A.; Hillmyer, M. A.; Tolman, W. B. *Biomacromolecules* **2007**, *8*, 3634-3640.
- Wang, S.; Vajjala Kesava, S.; Gomez, E. D.; Robertson, M. L. *Macromolecules* **2013**, *46*, 7202-7212.
- Ward, I. M.; Sweeney, J. *Mechanical Properties of Solid Polymers*, Wiley, Chichester, 3rd Edn., 2012.
- Warwel, S.; Brüse, F.; Demes, C.; Kunz, M.; Rüsch gen. Klaas, M. *Chemosphere* **2001**, *43*, 39-48.
- Warwel, S.; Brüse, F.; Kunz, M. *Fresenius' Environ. Bull.* **2003**, *12*, 534-539.
- Warwel, S.; Demes, C.; Steinke, G. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 1601-1609.
- Warwel, S.; Jägers, H. G.; Thomas, S. *Lipid/Fett* **1992**, *94*, 323-328.
- Warwel, S.; Tillack, J.; Demes, C.; Kunz, M. *Macromol. Chem. Phys.* **2001**, *202*, 1114-1121.
- Weiper-Idelmann, A.; aus dem Kahmen, M.; Schaefer, H. J.; Gockeln, M. *Acta Chem. Scand.* **1998**, *52*, 672-682.
- Weiss, A. In *Modern Biooxidation;* Schmid, R. D.; Urlacher, V. L., Eds.; Wiley-VCH: Weinheim, **2007**; 193-210.
- Wenzel, T.; Arriola, D.; Carnahan, E.; Hustad, P.; Kuhlman, R. in *Topics in Organometallic Chemistry*, *Vol. 26* (Ed.: Guan, Z.), Springer Berlin/Heidelberg, **2009**, pp. 65-104.
- Whiteley, K. S.; Heggs, T. G.; Koch, H.; Mawer, R. L.; Immel, W. Polyolefins. in *Ullmann's Encyclopedia of Industrial Chemistry*, *Vol. 14* (Eds: Gerhartz, W.; Elver, B.), Wiley-VCH, Weinheim, **2005**, pp. 1-103.
- Witt, T.; Mecking, S. *Green Chemistry* **2013**, *15*, 2361-2364.

- Witt, T.; Stempfle, F.; Roesle, P.; Häußler, M.; Mecking, S. *ACS Catal.* **2015**, *5*, 4519-4529.
- Woo, E. M.; Barlow, J. W.; Paul, D. R. *Polymer* **1985**, *26*, 763-773.
- Wunderlich, B. *Macromolecular Physics: Vol. 1.* New York: Academic Press, **1973**.
- Yadav, G. D.; Doshi, N. S. *Green Chem.* **2002**, *4*, 528-540.
- Yamamoto, M.; Witt, U.; Skupin, G.; Beimborn, D.; Müller R.-J. in *Biopolymers*; Eds. Steinbüchel, A.; Doi, Y. Wiley-VCH: Weinheim, **2002**; Vol. 4, pp 299-311.
- Yamamoto, Y.; Fujikawa, R.; Umemoto, T.; Miyaura, N. *Tetrahedron* **2004**, *60*, 10695-10700.
- Yang, Y.; Lu, W.; Zhang, X.; Xie, W.; Cai, M.; Gross, R. A. *Biomacromolecules* **2009**, *11*, 259-268.
- Yuki, Y.; Takahashi, K.; Tanaka, Y.; Nozaki, K. *J. Am. Chem. Soc.* **2013**, *135*, 17393-17400.
- Zhang, J.; Leitus, G.; Ben-David, Y.; Milstein, D. *Angew. Chem. Int. Ed.* **2006**, *45*, 1113-1115.
- Zhao, C.; Bruck, T.; Lercher, J. A. *Green Chem.* **2013**, *15*, 1720-1739.
- Zhu, Y.; Jang, S. H. A.; Tham, Y. H.; Algin, O. B.; Maguire, J. A.; Hosmane, N. S. *Organometallics* **2012**, *31*, 2589-2596.
- Zibek, S.; Wagner, W.; Hirth, T.; Rupp, S.; Huf, S. *Chem. Ing. Tech.* **2009**, *81*, 1797-1808.
- Ziegler, K.; Hechelhammer, W. *J. Liebigs Ann. Chem.* **1937**, *528*, 114-142.