Linear Semicrystalline Polyesters and Polyamides from Plant Oil Fatty Acids via Catalytic Alkoxycarbonylation

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‘He affirmed his significance as a conscious rational animal proceeding syllogistically from the known to the unknown and a conscious rational reagent between a micro- and a macrocosm ineluctably constructed upon the incertitude of the void.’

James Joyce, *Ulysses,* episode 17.

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Publications

Part of this work has been published:

Journal Publications

Florian Stempfle, Dorothee Quinzler, Ilona Heckler, Stefan Mecking*:
Long-Chain Linear C_{19} and C_{23} Monomers and Polycondensates from Unsaturated Fatty Acid Esters.
Macromolecules **2011**, *44*, 4159-4166.

Dorothee Quinzler, Stefan Mecking*:
Linear Semicrystalline Polyesters from Fatty Acids by Complete Feedstock Molecule Utilization.
Angew. Chem. Int Ed. **2010**, *49*, 4306-4308. *Angew. Chem.* **2010**, *122*, 4402-4404.
Selected as Very Important Paper by the Editors. Highlighted in David J. Cole-Hamilton: Nature's Polyethylene. *Angew Chem. Int. Ed.* **2010**, *49*, 8564-8566. *Angew. Chem.* **2010**, *122*, 8744-8746.

Dorothee Quinzler, Stefan Mecking*:
Renewable-resource based poly(dodecyloate) by carbonylation polymerization.
Chem. Commun. **2009**, 5400-5402.

Journal Publications in Proximity to this Work

Marc R. L. Furst, Ronan Le Goff, Dorothee Quinzler, Stefan Mecking, Catherine H. Botting, David J. Cole-Hamilton*:
Polymer precursors from catalytic reactions of natural oils.
Green Chem. **2012**, *14*, 472-477.

Justyna Trzaskowski, Dorothee Quinzler, Christian Bährle, Stefan Mecking*:
Aliphatic Long-Chain C_{20} Polyesters from Olefin Metathesis.
Macromol. Rapid Commun. **2011**, *32*, 1352-1365.

Poster Presentations

Dorothee Quinzler, Cécile Bouilhac, Anna Osichow, Christoph J. Dürr, Stefan Mecking*: Thermoplastic Polyesters from Plant Oils by Carbonylation Chemistry
Heidelberg Forum of Molecular Catalysis, Heidelberg, 6th November 2009.

Dorothee Quinzler, Cécile Bouilhac, Stefan Mecking*:
Thermoplastic Polyesters from Plant Oils by Carbonylation Chemistry
ProcessNet Tagung 'Industrielle Nutzung nachwachsender Rohstoffe',
Frankfurt am Main, 20th-21st January 2010.

Dorothee Quinzler, Cécile Bouilhac, Stefan Mecking*:
Thermoplastic Polyesters from Plant Oils by Carbonylation Chemistry
3rd Workshop on Fats and Oils as Renewable Feedstock for the Chemical Industry,
Emden, 14th-16th March 2010.

Dorothee Quinzler, Florian Stempfle, Ilona Heckler, Christoph J. Dürr, Philipp Roesle, Stefan Mecking*: Novel Hydrophobic Linear Semicrystalline Polyesters and Polyamides from Fatty Acids by Complete Feedstock Molecule Utilisation
Polymers in Biomedicine and Electronics - Biannual Meeting of the GDCh-Division, "Macromolecular Chemistry" and Polydays 2010, Berlin-Dahlem, 3rd-5th October 2010.

Conference talk

Dorothee Quinzler, Cécile Bouilhac, Christoph J. Dürr, Stefan Mecking*:
Semi-crystalline Polyesters from Plant Oils
MACRO 2010 - 43rd IUPAC World Polymer Congress, Glasgow, 11th – 16th July 2010.

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I Abbreviations

Methods

DSC	Differential Scanning Calorimetry
GC	Gas Chromatography
GPC	Gel Permeation Chromatography
NMR	Nuclear Magnetic Resonance
WAXS	Wide Angle X-ray Scattering

Compounds and Molecular Fragments

cod	cycloocta-1,5-diene
dba	dibenzylideneacetone
DMF	N, N-dimethylformamide
DMSO	dimethyl sulfoxide
dtbpp	1,3-bis(di-*tert*-butylphosphino)propane
dtbpx	1,2-bis[(di-*tert*-butylphosphino)methyl]benzene
EDTA	ethylenediaminetetraacetate disodium salt
Et	ethyl
HOAc	acetic acid
MTBE	methyl *tert*-butyl ether
Me	methyl
MeOH	methanol
$MeSO_3H$	methanesulfonic acid
OAc^-	acetate
OBu^-	butylate
O^tBu^-	*tert*-butylate
O^iPr^-	*iso*-propylate
PA	polyamide
PBS	poly(butyl succinate)
PET	poly(ethylene terephthalate)
Ph	phenyl
PHA	poly(hydroxy alkanoate)
PLA	poly(lactic acid)
PS	polystyrene
Py	pyridine
THF	tetrahydrofurane
tppts	tris(3-sodiumsulfonatophenyl)phosphine
xantphos	4,5-bis-(diphenylphosphino)-9,9-dimethylxanthene

Spectroscopy

br	broad
$^{13}C\{^1H\}$	CH decoupled ^{13}C-NMR
δ / ppm	chemical shift / parts per million
d	doublet

HMBC	Heteronuclear Multiple Bond Correlation
HSQC	Heteronuclear Single Quantum Correlation
$^{n}J_{A\text{-}B}$	J-coupling between nuclei A and B via n bonds
m	multiplet
q	quartet
s	singlet
t	triplet

Miscellaneous

calcd.	calculated
DP_n	degree of polymerisation
eq.	equivalents
M	molecular weight
Mtonnes	mega metric tons
M_n	number average molecular weight, $M_n = \frac{\sum_i n_i M_i}{\sum_i n_i}$
M_w	weight average molecular weight, $M_w = \frac{\sum_i w_i M_i}{\sum_i w_i} = \frac{\sum_i n_i M_i^2}{\sum_i n_i M_i}$
n.d.	not determined
p	functional group conversion
RT	room temperature
T_c	crystallisation temperature
T_m	melting temperature
vs.	versus
wt.-%	weight percent

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1 Introduction

In the long run resources of fossil fuels are running short. However, our modern life is strongly dependent on fossil fuels, not only as energy resource but also as starting material for modern life materials. According to information published by the trade association Plastics Europe, around 280 million tonnes of plastics were produced worldwide in 2011,[1] equating to around 6 % of the global oil consumption.[2] At first glance this appears to be a relatively small figure. However, the demand for plastics keeps growing rapidly, represented by the long term trend of world plastics production growth of almost 5 % per year over the past 20 years (cf. Figure 1.1), a trend which is expected to continue and to further increase.

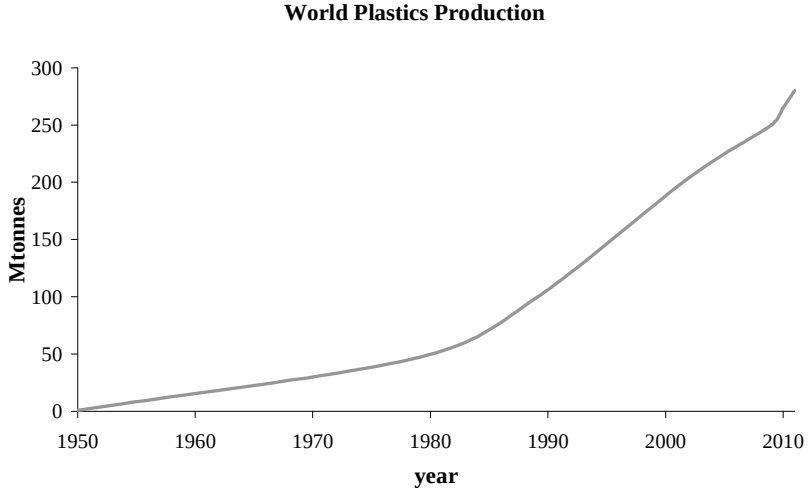


Figure 1.1 World plastics production from 1950 to 2011.[1]

While for energy resources the utilisation of many alternative resources to fossil fuels like solar, wind and geothermal energy is already established, only a limited number of renewable resource based plastics are known to date. Therefore it seems to be even more important to search for alternative resources for plastics production and also to develop new renewable resource based materials. The increased and sustainable utilisation of renewable resources can not only reduce our consumption of and dependence on fossil fuels but may also reduce our carbon dioxide emissions thus contributing to climate protection.[3-4] However, a critical assessment is necessary for each individual case as renewables are not per se advantageous with regard to these issues.

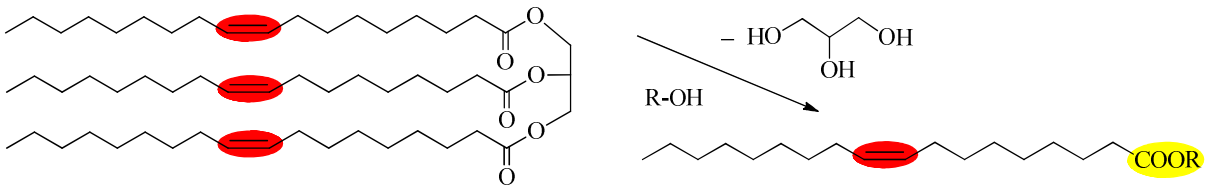
So far, the production of thermoplastics from renewable resources usually involves a fermentation step which is also the case for poly(lactic acid) PLA and poly(hydroxy alkanoates) PHAs, the most well-known and most common plastics from renewable resources

to date.[3-7] Fermentation steps, however, mostly deliver rather limited space-time yields making it difficult for products of such processes to compete with products of petrochemical processes on commercial terms.[5] In this context the production of sugar cane based polyethylene which was introduced in 2010 by Braskem is also remarkable.[8]

1.1 Plant Oils as Renewable Feedstock

Although plant oils account for only about 2 % of the annually produced biomass, roughly 35 % of the renewable feedstocks currently utilised by the chemical industry are based upon fatty acids.[9] They are in principle attractive substrates for the chemical synthesis of many different products such as lubricants, engine oils, cosmetics, detergents and plastics as they exhibit a unique structure with long linear methylene sequences, in this sense somewhat similar to fossil fuels, but with an additional terminal functional group. [10-13] Furthermore, many oil crops contain a single type of fatty acid in very high contents, like oleic acid in high oleic sunflowers or ricinoleic acid in castor beans, also owing to intelligent breeding. This hugely simplifies the recovery of the desired fatty acids in high purities. A long-standing utilisation of a fatty acid renewable feedstock is for example illustrated by the preparation of the difunctional monomer sebacic acid from ricinoleic acid,[14] which is converted to aliphatic polyamides like Nylon-6,10 with a beneficially low water uptake. Like in this application, cleavage reactions like ozonolysis or catalytic oxidation of the olefin in unsaturated fatty acids yield α,ω-dicarboxylic acids and derivatives of medium chain length along with monofunctional oxygenates as a stoichiometric byproduct which quite often represent molecules of limited industrial interest. Other industrially applied transformations of fatty acids include hydrogenation, isomerisation, dimerisation and olefin metathesis, to list the most important ones for the sake of completeness.[9, 15] Another route to α,ω-dicarboxylic acids from plant oils is fermentative ω-oxidation in which the entire fatty acid chain remains intact.[16-18] However, this process also suffers from limited space-time yields and complicated work up of the product reaction mixture.[18-19] So far, the major use of entire plant oil triglycerides in polymers is in polyurethanes or epoxy resins in which they serve as multifunctional cross-linkers.[20-22] With regard to their complete utilisation as monomers in thermoplastics production unsaturated plant oils provide, after transesterification or hydrolysis with liberation of glycerol, long-chained molecules with two functional groups which are accessible to chemical reactions. However, the double bond is located in the centre of the molecule (Scheme 1.1). For complete utilisation of fatty acids in the generation of

crystallisable linear thermoplastics by step-growth polymerisation, a functionalisation at the chain end is required.



Scheme 1.1 Functional groups in plant oils and fatty acid esters.

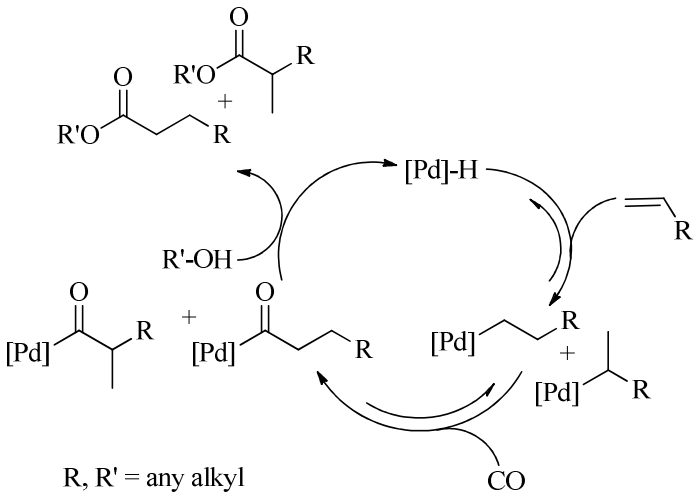
1.2 Alkoxycarbonylation

A useful reaction which converts olefins into ester groups is the alkoxycarbonylation reaction.[23-27] Here, the olefin reacts with carbon monoxide and an alcohol to form an ester in the presence of a suitable catalyst. The alkoxycarbonylation reaction has been studied for a variety of olefins and alcohols, but most extensively for ethylene and methanol. This process has also been commercialised by Lucite International, in the so called Alpha process, a novel route to methylmethacrylate practised on a 120 000 t/annum scale. Ethylene, methanol and carbon monoxide are reacted in the presence of a homogeneous palladium(II)/diphosphine catalyst to form propanoic acid methyl ester which is further reacted with formaldehyde in the presence of a solid SiO_2 catalyst to form methylmethacrylate at a, according to the producer, 30-40 % cheaper price than conventionally produced methylmethacrylate. Further advantages of the Alpha process are, that virtually no waste is produced and that the feedstocks employed can potentially be made from biomass. The palladium catalyst for alkoxycarbonylation reaction in the first step displays very high selectivity with excellent activity and due to its full solubility in the reaction mixture it can be continuously recycled to the reaction stage.[28-30]

In general, for the alkoxycarbonylation reaction many different transition metal catalyst systems based on Ni, Fe, Ir, Co, Rh, Ru, Pt and Pd are known. However, the cobalt, platinum and palladium based systems form the most selective catalysts towards alkoxycarbonylation with relatively mild reaction conditions for the noble metals. A competing reaction is the formation of polyketones.[23, 31-33]

Mechanistic studies of the alkoxycarbonylation reaction were mainly conducted with palladium and platinum complexes as cobalt complexes are paramagnetic, which makes them unsuitable for NMR spectroscopic studies. It is widely accepted that palladium/phosphine catalysed alkoxycarbonylation of olefins involves a palladium(II)hydride species. The

commonly accepted catalyst cycle is depicted in Scheme 1.2.[34-36] Migratory insertion of 1-olefins in either 1,2- or 2,1-fashion produces either linear or branched palladium-alkyls. Therefore also two palladium-acyl products, a branched and a linear, can occur after carbon monoxide insertion and a branched and linear ester product after nucleophilic attack of an alcohol. In this catalytic cycle all steps are reversible except for the nucleophilic attack of the alcohol, the so called alcoholysis, which is also considered to be the rate determining step of the reaction.[37]

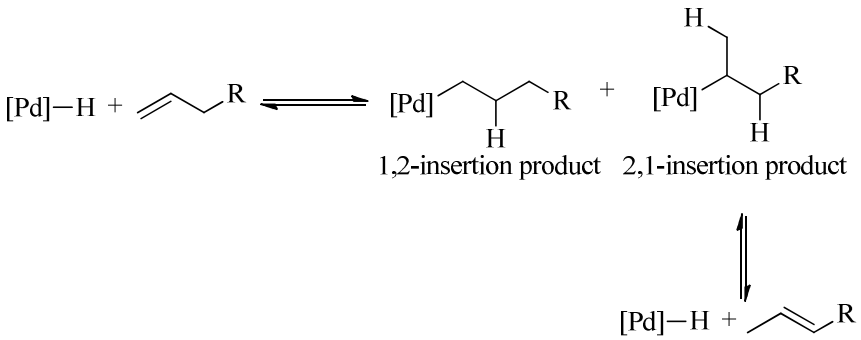


Scheme 1.2 Generally accepted mechanism of the Pd-catalysed alkoxycarbonylation.

When applying 1-olefins in the reaction the two different modes of olefin insertion into the metal-hydride bond also lead to different products from β-hydride elimination (Scheme 1.3). In case of 2,1-insertion of the olefin into the metal-hydride bond isomerisation of the double bond can occur after β-hydride elimination. This can convert the 1-olefin into the thermodynamically more stable internal olefin. On the other hand in case of internal olefins as a substrate, repeated β-hydride elimination can in principle lead to linear metal-alkyls and thus to the linear ester products.

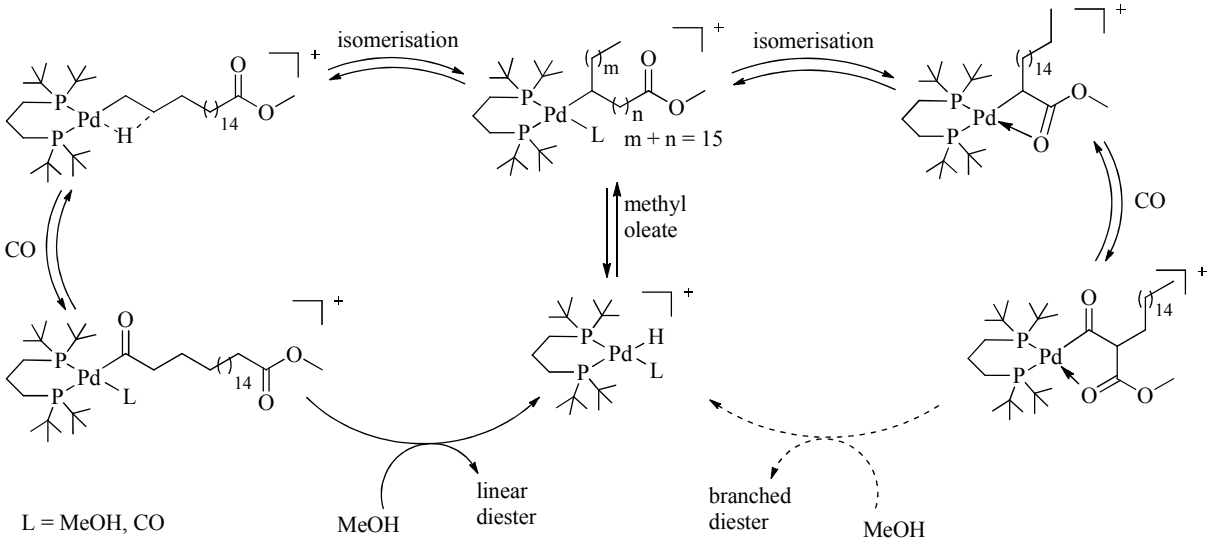
As previously illustrated, a whole range of different trialkyl phosphine ligands are suitable for the palladium catalysed alkoxycarbonylation.[36, 38-43] In general, there are two different classes of phosphine ligands which are active in alkoxycarbonylation, monophosphines and chelating diphosphines. They are all relatively electron rich and carry bulky substituents. The application of palladium complexes carrying monodentate phosphine ligands tends to lead to a higher regioselectivity towards the branched carboxylic ester products whereas the use of bulky chelating ligands results in a greatly improved regioselectivity towards linear

carboxylic esters.[41] Notably, diphosphines of intermediate steric bulk like 1,3-bis(diphenylphosphino)propane will promote chain growth to polyketones.[44]



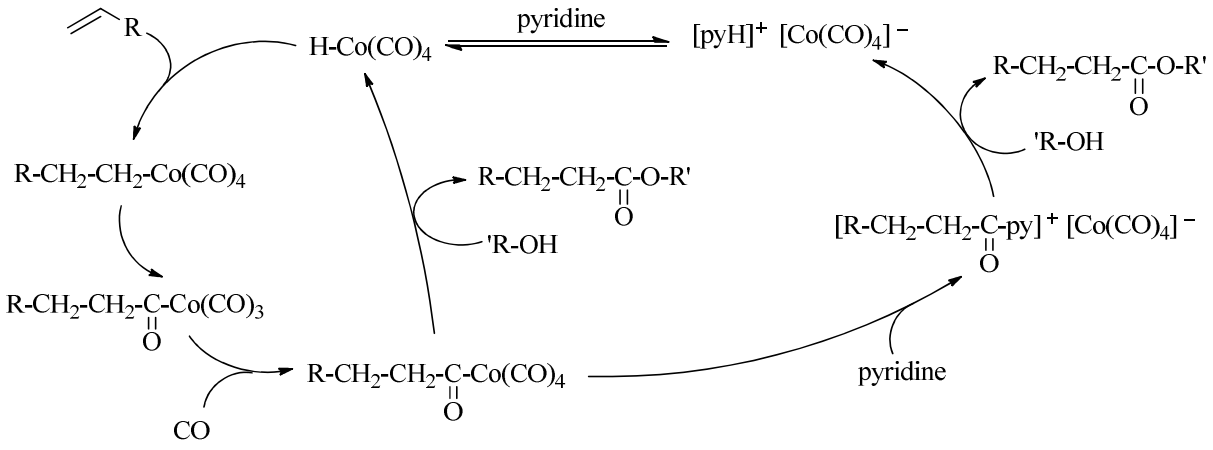
Scheme 1.3 Mechanism for 1-olefin isomerisation via β-hydride elimination.

Recently, mechanistic insights into the palladium catalysed isomerising alkoxycarbonylation of methyl oleate were reported and the reaction pathways depicted in Scheme 1.4 were observed. In isomerising alkoxycarbonylation the double bond deep inside the molecule is isomerised to the chain end and then carbonylated to form the linear diester product (cf. Scheme 5.1). The strong preference of linear palladium alkyls over branched palladium alkyls is related to the extremely bulky diphosphine ligand dtbpp employed in this study, which restricts the available space around the other two coordination sites of the square-planar metal centre, and favours methanolysis of the linear acyl.[45]



Scheme 1.4 Decisive pathways of the isomerising alkoxycarbonylation of methyl oleate with dtbpp.

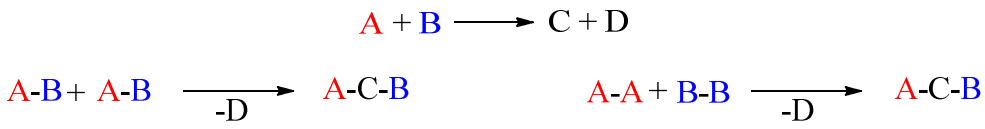
The cobalt-catalysed alkoxycarbonylation reaction has mainly been studied for the double methoxycarbonylation of buta-1,3-diene to form dimethyl adipate[32, 46-48] for use as an intermediate in nylon-6,6 manufacture. This process has been developed and operated on a pilot-plant scale by BASF.[49] It is assumed that the first step in the cobalt-catalysed alkoxycarbonylation involves the insertion of an olefin into a cobalt-hydride species and the subsequent formation of a cobalt-acyl species. However, in the cobalt-catalysed alkoxycarbonylation also a catalytic promoter, usually a nitrogen-base is present. Pyridine has proven to be the most effective catalytic promoter in terms of higher conversions and selectivity towards the linear ester products. It is widely accepted that the catalytic promoter significantly accelerates the alcoholysis reaction which is considered the rate determining step (Scheme 1.5).[47, 50-52] In fact, the dependence of the overall reaction rate on the pyridine concentration is described by a characteristic curve with a maximum.[53] The cause thereof lies in the equilibrium between $H\text{-}Co(CO)_4$ and $[PyH]^+[Co(CO)_4]^-$ which forms in the presence of pyridine. By increasing the pyridine concentration above a certain level, the alcoholysis no longer is the rate determining step but the insertion of olefin into the $H\text{-}Co(CO)_4$ due to its reduced concentration. In general there is relatively little definitive experimental evidence in support of mechanistic pathways, largely because of the lack of readily available spectroscopic 'handles' to monitor metal complex speciation in solution under reaction conditions.[32] Therefore the discussion on the mechanism is ongoing.



Scheme 1.5 Postulated mechanism of the Co-catalysed alkoxycarbonylation – only formation of linear product is shown.

1.3 Condensation Polymerisation and Step-growth Polymers

Condensation polymerisation follows a step-growth mechanism in which the formation of oligomers precedes polymer formation. The step growth polymerisation kinetic originally described by Carothers[54] and Flory[55] means that all reactive species in a reaction mixture (monomers, linear oligomers and polymers) can react with each other at any time and at any concentration. For the formation of linear polycondensates from bifunctional monomers two routes are possible: one can either start from one type of monomer bearing two different types of functional groups which can undergo a condensation reaction (AB-Type condensation polymerisation) or from two different bifunctional monomers bearing two identical functional groups each, which can also undergo a condensation reaction (A_2B_2-Type condensation polymerisation, Scheme 1.6).[55-56]



Scheme 1.6 AB-Type and A_2B_2-Type condensation polymerisation

For achieving any substantial molecular weights in polycondensation reactions highly pure monomers are a prerequisite, owing to the correlation $DP_n = 1/(1 - p)$, the so called Carothers equation between the degree of polymerisation (DP_n) and the functional group conversion (p).[55, 57] In the case of the A_2B_2-Type condensation the degree of polymerisation is not only determined by the functional group conversion but also by the exact stoichiometry of the reacting functional groups A and B. Even if an exact stoichiometry of these functional groups is provided at the beginning of a polycondensation reaction it is possible that during the ongoing reaction this exact stoichiometry cannot be maintained due to side reactions, sublimation or evaporation of one of the reactants. The formation of macrocycles is also a non-negligible side reaction, especially at the end of the polymerisation reaction, when the concentration of remaining functional groups is relatively small thus representing highly diluted reaction conditions ideal for cyclisation.[55]

Furthermore it has to be taken into account that condensation reactions involve equilibria and that the value of the equilibrium constant also affects the functional group conversion and therefore the degree of polymerisation.[56] Assuming dynamic equilibria for the condensation polymerisations illustrated in Scheme 1.6 the following expression can be formed.

$$K = \frac{[-C-]\cdot[D]}{[A-]\cdot[B-]}$$

For the polyesterification of e.g. 1 mol hydroxyl groups (1/2 mol diol) and 1 mol carboxylic acid ester (1/2 mol dicarboxylic acid ester), according to Schulz[58] and Flory[55], this expression can be transformed into:

$$K = \frac{p \cdot n_D}{(1-p)^2}$$

There n_D is the amount of alcohol in mol present in the reaction mixture. When solving this equation for p the upper limit for the functional group conversion, depending on the ratio $\beta = K/n_D$, can be obtained:

$$p = \frac{1}{2\beta}\left(1 + 2\beta - \sqrt{1+4\beta}\right)$$

With the Carothers equation this expression leads to the maximum degree of polymerisation limited by the dynamic equilibrium:

$$DP_n = \frac{2\beta}{\sqrt{1+4\beta}-1}$$

Usually a very high functional group conversion is desired with values of p close to 1. The equation can thus be simplified to:

$$DP_n \cong \sqrt{\beta} = \sqrt{K / n_D}$$

That means that the degree of polymerisation merely depends on the value of the equilibrium constant and the amount of alcohol present in the reaction mixture. The larger the equilibrium constant and the smaller the alcohol concentration the higher is the degree of polymerisation. Unfortunately, this means that if the equilibrium constant is in the range of 1-10, which it generally is for common polyesterification reactions, mole fractions as low as a promille of alcohol in the reaction mixture prevent the formation of high molecular weight polymers. For this purpose an efficient removal of the liberated small molecule (e.g. methanol) is very important. In most instances this is achieved by either using low pressures of typically 0.1-0.5 mbar or by applying a dry nitrogen purge at high temperatures. Also efficient agitation and customised reactor design for the efficient removal of condensates is required. This is especially important in melt polymerisation processes as molecular weight increases with conversion and thus the melt viscosity increases dramatically and the requirement for efficient agitation and condensate removal becomes more difficult and thus more important.[59] Condensation polymerisation is not only of academic interest. Important thermoplastics like

PET and PA 6 6 are manufactured by condensation polymerisation on an industrial scale. In general, step-growth polymers such as polyesters and polyamides possess more robust mechanical properties, including toughness in combination with stiffness and higher temperature resistance than polymers from chain growth polymerisation processes such as polyolefins and other vinyl-derived polymers. But most step-growth-based polymers are also more expensive than various vinyl-based structures. This is, at least in part, due to the cost of the monomers used in step-growth polymerisations, which require several steps from the bulk commodity petrochemical intermediates to the polymerisable monomer.[60]

The physical properties of polymers are primarily determined by their molecular weight and chemical composition. Achieving high molecular weights during polymerisation is critical if the polymer is to have sufficient thermal and mechanical properties to be useful. Below a critical molecular weight, properties such as tensile strength and melt and crystallisation temperature are lower. As the molecular weight increases beyond that critical molecular weight, changes in thermal properties are not as significant. Thermoplastic commercial step-growth polymers such as polyesters, polycarbonates and polyamides are generally made with number average molecular weights in the range of 10,000-50,000 g mol^{-1}. Polymers within this molecular weight range are generally strong enough for use as structural materials yet low enough in melt viscosity to be processable at a reasonable cost.[60]

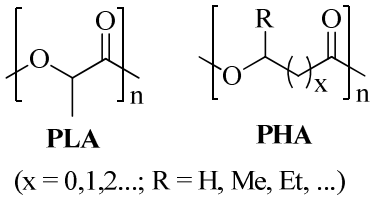
1.4 Aliphatic Polyesters

As thermoplastics, aliphatic polyesters have long been of minor importance due to their low hydrolytic and chemical resistance and low melting temperatures, which can all be related to a low crystallinity. They have mainly been applied as plasticizers or macromonomers for the preparation of polyurethane foams, coatings or elastomers. Hydrolytic sensitivity, however, is a requested feature for the design of environmentally degradable plastics and biomedical polymers. For this purpose aliphatic degradable polyesters or copolyesters, either of natural or synthetic origin, have been the subject of intense academic and industrial attention during the past two decades.[6, 59]

The most prominent examples are poly(lactic acid) PLA and poly(hydroxy alkanoates) PHAs which are not only biodegradable but also bio-based. PLA is made from glucose by its fermentation to lactic acid, which could be subjected to direct polycondensation but normally is first chemically converted to lactide, a cyclic dimer of lactic acid. The lactide is converted by ring opening polymerisation to PLA which is mainly utilised in packaging and medical

applications. As lactic acid exhibits a stereogenic centre the crystallinity of the final polyester is heavily influenced by the relative amounts of the different stereoisomers. In this way the properties of the polymer can be adjusted to satisfy the needs of different applications. Nevertheless, PLA suffers from a low heat distortion temperature, a low impact strength and poor barrier properties. However, PLA is not quite a typical representative of the class of aliphatic polyesters, as in PLA the ester moieties dominate polymer properties like the melting point.

PHAs are structurally closely related to PLA as they are also branched polyesters but with higher content of aliphatic chains (Scheme 1.7). PHAs are made from sugars, starch or fatty acids, not by chemical synthesis but by various microorganisms as a carbon and energy storing substance. Their great structural variety gives rise to multitude different property profiles and different possible applications.[61]



Scheme 1.7 Structure of poly(lactic acid) and general structure of poly(hydroxy alkanoates).

Other industrially proven aliphatic polyesters are the fossil fuel based poly(ε-caprolactone) and poly(butylene succinate). Poly(ε-caprolactone) is mostly used in blends due to its low modulus and low melting point. Poly(butylene succinate) however is relatively stiff. Dicarboxylic acids with longer hydrocarbon chains lead to more flexible materials. All aliphatic polyesters, bio-based or not, are prone to chemical and microbial hydrolysis.[61] The degradation rate is influenced by the molecular weight, crystallinity, hydrophobicity and the glass transition temperature of the polyester, by the degradation conditions and by the presence of degradation products.

The backbone structure of a polymer to a large extent defines the flexibility and stability of a polymer molecule. Consequently, a great range of polymer properties can be achieved within each class of step-growth polymers by varying the backbone structure using different monomers. In aliphatic polymers the concentration of the linking groups (e.g. ester or amide) in the backbone greatly influences the physical properties. Increasing the methylene content in polyesters (except for the very short chain representatives like PLA and PBS) also increases

the melting point eventually tending towards the T_m of polyethylene at low linking group concentrations.[59] However, the melting temperatures in aliphatic polyesters are not only affected by the total number of methylene groups in the repeat unit but also by their position between the ester groups. In general, polyesters of even numbered diols and dicarboxylic acids exhibit higher melting temperatures than those of odd numbered glycols and dicarboxylic acids.[62]

1.5 Aliphatic Polyamides

In general, there are two main types of polyamides, the AB-type polyamides from ω-aminocarboxylic acids or, like in the case of PA 6, lactams and the AABB-type polyamides from diamines and dicarboxylic acids. A simple system of nomenclature designates these polyamides (PA) by the number of carbon atoms in the monomers. Two numbers represent an AABB-type polyamide, the first number referring to the number of carbon atoms in the diamine and the second number to the number of carbon atoms in the dicarboxylic acid monomer. An AB-type polyamide is represented by a single number.[63] Even and odd numbered AB-type polyamides and even-even, odd-odd, even-odd and odd-even numbered AABB-type polyamides exhibit to some extent different polymer properties. This is due to the different degree of order in the crystalline phase. The order in the crystalline phase and the properties of polyamides in general are determined by the hydrogen bonds formed by –NH– and –CO– groups between neighbouring polymer chains.[64] Even-even polyamides like PA 6 6 and PA 6 10 primarily form crystal structures composed of sheets of fully extended planar chain segments joined by hydrogen bonds at room temperature. At room temperature polyamides containing odd numbers of methylene groups primarily form crystal structures similar to the pleated sheet structures of polypeptides.[65-67]

In the solid state usually less than 1 % of the amide groups in polyamides do not form hydrogen bonds.[68] This leads to a highly suppressed mobility of the polymer chains which predominates polymer properties.[63] The most obvious influence of the ratio between methylene and amide groups is the melting temperature of the polyamides and to some extent intermolecular hydrogen-bonding is also present in the melt.[68] Therefore the melting temperatures of polyamides decreases with increasing methylene group content, and polyamides containing odd numbers of methylene groups exhibit lower melting temperatures than polyamides with even numbers of methylene groups. In AABB-type polyamides with the same ratio of methylene groups to amide groups the polyamide with the biggest difference in

methylene group content of acid and amine component exhibits the highest melting temperature whereas the polyamide with an equal distribution of methylene groups between acid and amine component exhibits the lowest melting temperature. PA 4 10 with 250 °C exhibits a considerably higher melting point than PA 6 8 with 232 °C, both having a total of 12 methylene groups.[69]

The mechanical properties of common polyamides also strongly depend on their water content. In general, the higher the methylene content in a polyamide, the lower is its capability of absorbing water and the more independent are their specific volume mechanical properties of the water content.[70] Furthermore, the higher the methylene group content the higher the flexibility and the lower the heat resistance of the polyamide.[69] Plant-oil-based polyamides tend to have higher methylene group content than their fossil fuel based relatives. Different from most other bio-based polymers plant-oil based polyamides are considered engineering plastics. They offer new, desirable properties which have currently not been achieved by fossil fuel based polyamides and they are established even in the technically very demanding application fields of the automobile industry.[71] The first commercially available plant-oil-based polyamide was PA 11 which was introduced into the market under the trade name ‘rilsan’ in 1955. PA 11 is based on ricinoleic acid, which can undergo a thermolytic cleavage under the formation of heptaldehyde and undecenoic acid (Scheme 3.1). Undecenonic acid can further be transformed in a two step conversion into 11-aminoundecanoic acid, which can be subjected to polycondensation.[72]

Further, at least partially bio-based polyamides, are PA 10 10 (100 % bio-based), PA 6 10 (62 % bio-based) and PA 10 12 (45 % bio-based). They are all based on sebacic acid and are tested, approved and to some extent even already employed in hydraulic connector lines, pneumatic brake lines or fuel lines.[71] Sebacic acid is also derived from ricinoleic acid but by alkaline cleavage under pressure and high temperature leading to the formation of sodium sebacate and 2-octanol.[73] In contrast to aliphatic polyesters all aliphatic polyamides, also the bio-based ones, are considered non-biodegradable.[74]

2 Objective

Today’s polymer production relies almost exclusively on fossil feedstocks. This applies particularly to thermoplastic polymers, which represent the largest type of industrial polymers before thermosets and elastomers. In view of the limited range of fossil feedstocks, polymers prepared from alternative renewable resources are desirable on the long term. Fatty acids from plant oils are attractive substrates for polymers as they contain long chain linear segments.

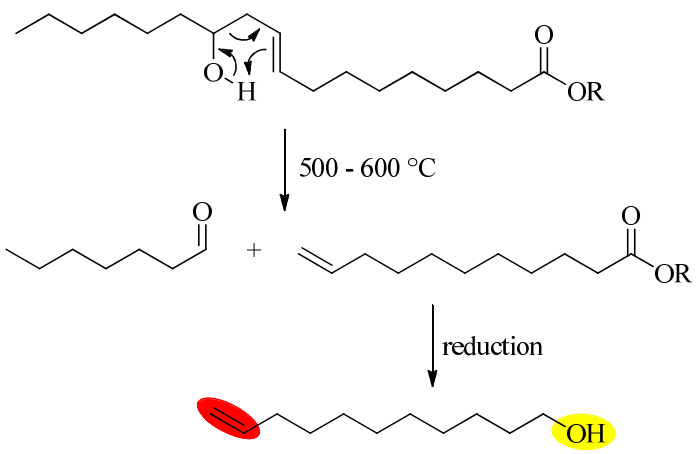
Although prices for ethylene and naphta have been continuously increasing over the last years, "almost as good as" replacements of existing fossil feedstock based products with products made from renewable resources will be difficult to achieve. Therefore the performance profile of plant oil based materials should be geared towards specific applications which are ideally unique to this feedstock.

In this context the aim of this work was to synthesise novel, plant oil based aliphatic polycondensates by means of the alkoxycarbonylation reaction. This required, amongst others, the finding of suitable catalyst systems and reaction conditions for different alkoxycarbonylation reactions and the finding of suitable transformation reactions for obtaining other difunctional monomers from the dicarboxylic acid esters synthesised by alkoxycarbonylation reactions.

3 Poly(dodecyloate) by Carbonylation Polymerisation of 10-Undecen-1-ol

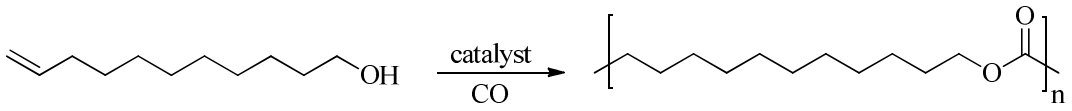
Thermoplastic polymers are currently prepared almost exclusively from fossil feedstocks. In view of their limited range, alternative renewable resources are desirable in the long term.[5] By comparison to routes employing a fermentation step, chemical synthetic routes in which the original molecular structure of the plant biomass employed is substantially retained are attractive as they can be efficient in terms of feedstock utilisation and reaction space-time yields, and provide novel properties. Polyesters are one of the most important classes of organic polymers, and indeed the more recently developed and commercialised biomass-based polymers are thermoplastic polyesters.[6]

Among the well known and common fatty acids ricinoleic acid, the major component of castor oil, is special as it has a hydroxylfunctionality at the C12 position. Therefore it can undergo a thermally induced rearrangement reaction which leads to heptaldehyde and undecenoic acid[75-76] which can be further reduced to 10-undecen-1-ol (Scheme 3.1).[14]



Scheme 3.1 Thermolytic cleavage of ricinoleic acid to produce 10-undecen-1-ol.

10-undecen-1-ol is a very interesting starting material for polyester synthesis as it bears a hydroxyl and olefin group at the ends of a rather long hydrocarbon chain. Alkoxycarbonylation of ω-unsaturated alcohols is a known route to lactones [77-80] by ring closure, but in principle it can also resemble an AB step growth polymerization (Scheme 3.2). For 10-undecen-1-ol, reaction with CO catalysed by Pd(II)-salts modified with PPh_3 has been noted to yield oligomers without further details.[81-83]



Scheme 3.2 Poly(dodecyloate) by alkoxycarbonylation polymerisation of 10-undecen-1-ol.

3.1 Cobalt-catalysed Carbonylation Polymerisation

Of the variety of catalyst systems known for alkoxycarbonylation, cobalt catalysts are attractive as they are very robust and do not require costly phosphine ligands or noble metals, which are also sensitive to irreversible reduction to elemental metal in any reaction involving carbon monoxide. They are also not substrate-sensitive, are reactive towards higher alcohols other than methanol and, more importantly, internal olefins.[53, 84-85] Olefin isomerisation via β-hydride elimination is an ubiquitous reaction in the presence of transition metal compounds. While the formation of a small amount of unreacted internal olefin is unproblematic in a synthesis of small molecules, in the polymerization reaction studied a few percent of unreactive functional groups would severely limit molecular weights.

Exposure of neat 10-undecen-1-ol to carbon monoxide pressure at elevated temperature in the presence of catalytic amounts of $[Co_2(CO)_8]$/pyridine resulted in quantitative conversion to solid polymeric material (Scheme 3.2). Remarkably, in view of the high degree of functional group conversion required, and the high viscosity of polymer melts which might hamper further reaction at higher conversions, GPC demonstrates the material to be higher molecular weight polymer (Figure 3.1).

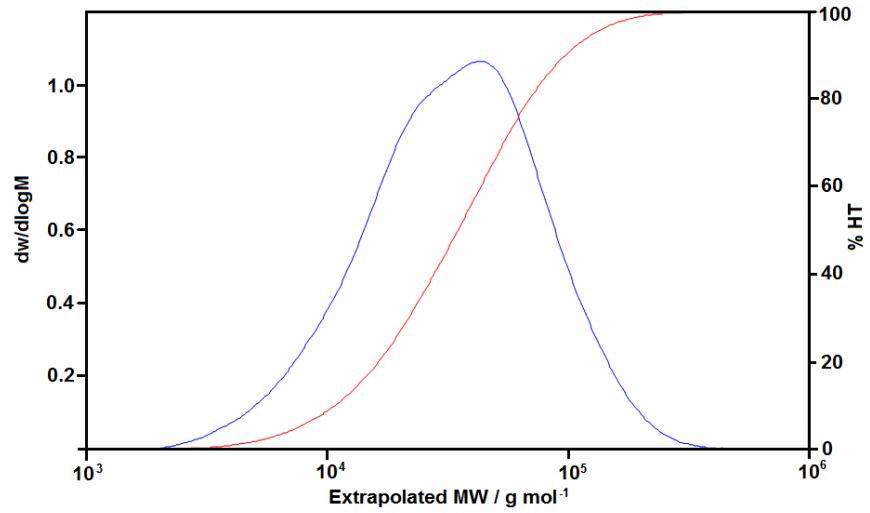


Figure 3.1 GPC trace of poly(dodecyloate) (in THF vs. PS standards) (Table 3.1, entry 10).

600 MHz ^{1}H-NMR spectra acquired with a highly sensitive cryogenic coil probe enabled the quantitative observation of internal olefin and hydroxy endgroups (Figure 3.2). A functional group conversion of up to > 99 % is evident from the methylene protons of the –CH_2OH endgroups. This corresponds to degrees of polymerization (DP_n) of > 100 (Table 3.1). The respective M_n values reasonably agree with apparent M_n from GPC vs. polystyrene standards. This also demonstrates that no excessive formation of macrocylic lactones occurred.

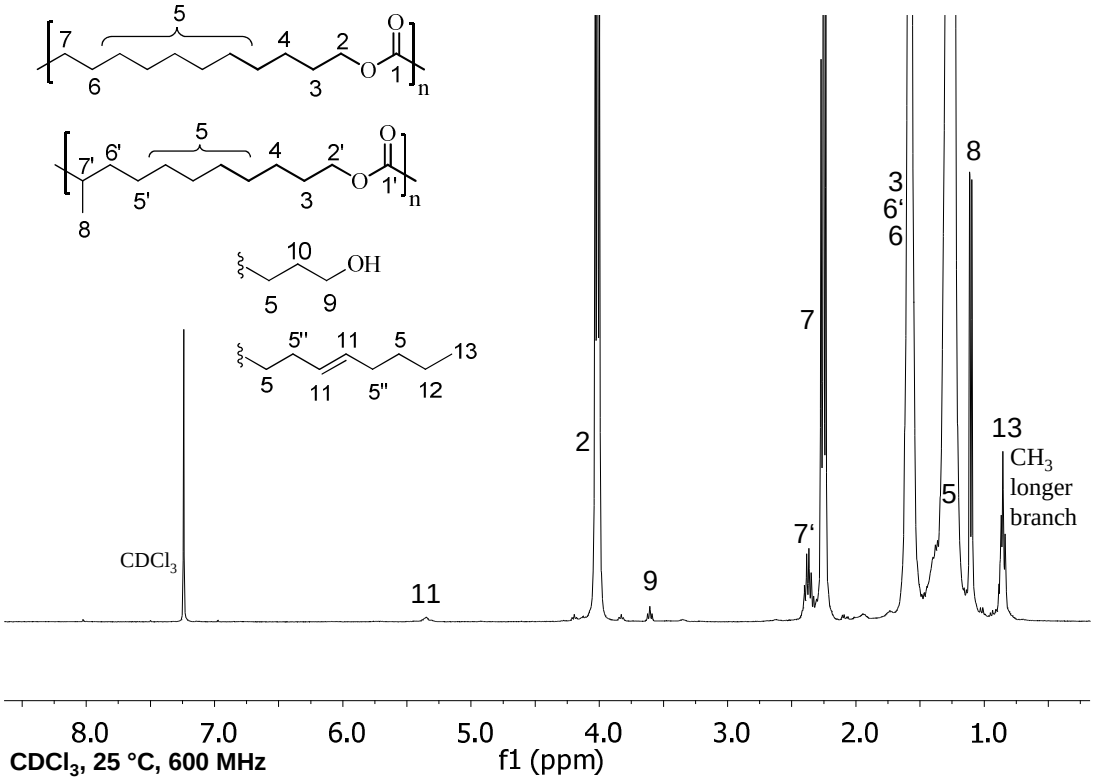


Figure 3.2 ^{1}H-NMR spectrum of poly(dodecyloate) prepared with [$Co_2(CO)_8$]/pyridine catalyst.

The influence of catalyst composition and reaction conditions on the polymerization reaction was studied (Table 3.1). The pyridine to Cobalt ratio has a moderate but significant effect on the degree of functional group conversion and consequently molecular weight (entries 1, 3 and 4). A 32 fold excess of pyridine appears optimum which is in agreement with the findings for the cobalt catalysed alkoxycarbonylation of other substrates. In the range of pressure studied, up to 200 bar, an increased CO pressure favours the polymerization reaction, and promotes formation of higher molecular weight polymer. Similar to trends observed in the alkoxycarbonylation of 1-olefins to small molecule products,[53] a temperature around 160 °C appears beneficial. At 100 °C only oligomers are formed, presumably due to a slower polymerization reaction, and at 200 °C also comparably lower molecular weight polymer was

formed, likely due to catalyst decomposition.[84] Reaction with added solvent (toluene) resulted in lower molecular weights, the unfavourable lower concentration of functional groups apparently dominates over a conceivable increased reactivity due to the higher mobility in the less viscous solution (entry 2). In this study, reactions were usually run for ca. 65 h to ensure the maximum degree of polymerization achievable. However, already after 16 h the reaction seems to be near completion (entry 9). $[Co_4(CO)_{12}]$ as a metal source was reported to afford higher yields in the preparation of carboxylic acid esters than $[Co_2(CO)_8]$,[85] in our hands under the conditions of the polymerization reaction no significant difference was observed (entry 3 vs. 10).

Table 3.1 Polymerisation results of the cobalt catalysed carbonylation polymerisation of 10-undecen-1-ol.

entry	pyridine / mmol	pyridine : Co	P / bar	T / ° C	t / h	$M_w \times 10^4$ (GPC) [d] / g mol^{-1}	$M_n \times 10^4$ (GPC) [d] / g mol^{-1}	DP_n (NMR)	T_m / °C
1	39	8 : 1	200	160	69	2.5	1.0	57	56 / 61
2[b]	11	8 : 1	200	160	64	0.4	0.2	12	55
3	154	32 : 1	190	160	65	4.7	2.2	140	61 / 66
4	307	64 : 1	200	160	69	2.2	1.1	40	62 / 66
5	154	32 : 1	180	100	67	n.d.	n.d.	n.d.[e]	n.d.
6	154	32 : 1	200	200	66	0.8	0.6	21	61 / 66
7	154	32 : 1	100	160	64	1.1	0.7	38	64 / 69
8	154	32 : 1	50	160	64	0.3	0.3	13	63
9	154	32 : 1	200	160	16	2.6	1.3	50	63 / 70
10[c]	154	32 : 1	190	160	67	4.6	2.3	146	n.d.

Polymerisations were performed in a 280 mL stainless steel autoclave using 0.175 mol undecenol and 2.4 mmol $[Co_2(CO)_8]$. [b] 50 mmol undecenol, 25 mL toluene, 0.7 mmol $[Co_2(CO)_8]$. [c] 1.2 mmol $[Co_4(CO)_{12}]$. [d] in THF vs. polystyrene standards. [e] 19 % conversion of the functional groups.

For enabling a detailed microstructure analysis via NMR spectroscopy residual cobalt had to be removed from the polymer due to its paramagnetism. This was achieved by extraction of dichloromethane solutions of the respective polymer with aqueous EDTA-solution which was acidified with HCl and mixed with small amounts of hydrogen peroxide. The thus obtained cobalt-free polymer samples were dissolved in $CDCl_3$ and good quality ^1H- and ^{13}C-NMR spectra could be obtained. About 20 to 30 % of the repeat units are branched, as a result of 2,1-insertion of terminal olefinic moieties, or reaction of internal olefinic groups formed by isomerisation. However, methyl branches predominate (Figure 3.3).

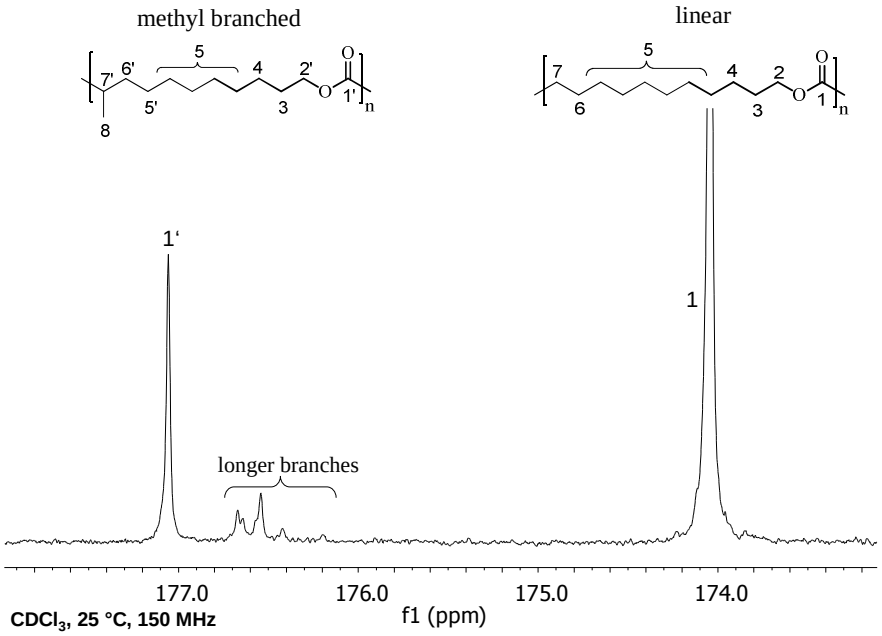


Figure 3.3 Carbonyl region of the $^{13}C\{^{1}H\}$-NMR spectrum of poly(dodecyloate) prepared with $[Co_2(CO)_8]$/pyridine catalyst.

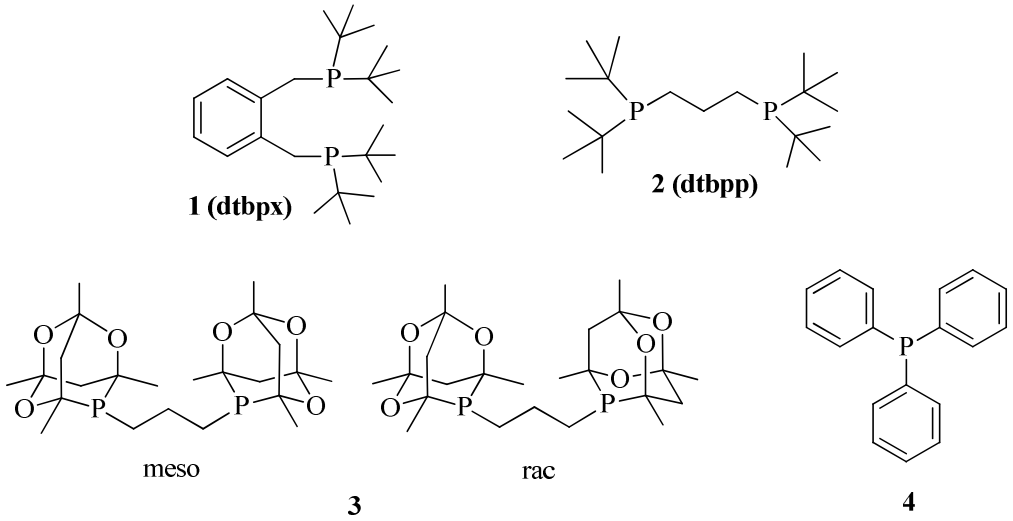
The polyesters obtained are semicrystalline with a complex melt behaviour, two melting peaks occur at around 65 °C. A narrow crystallisation transition is observed at T_c ca. 45 °C upon cooling. Molecular weights are in a regime where the thermal properties of the polyester are independent of molecular weight (Table 3.1). The similar melt behaviour of the different samples indicates that polymer microstructures do not differ substantially.

In conclusion, cobalt-catalysed reaction of 10-undecen-1-ol with carbon monoxide is a convenient route to higher molecular weight polyesters and the starting materials can be readily prepared from renewable resources. In this entirely chemical polyester synthesis, not involving fermentation, the molecular structure of the plant oil feedstock is largely retained in the linear polyester product, which predominantly consists of moderately branched hydrocarbon repeat units.

3.2 Palladium-catalysed Carbonylation Polymerisation

As illustrated above, cobalt/pyridine catalysed alkoxycarbonylation polymerisation of 10-undecen-1-ol is a versatile route to higher molecular weight polyesters with around 20 to 30 % of methyl- and higher branches adjacent to the carbonyl group of the ester moiety. However, the control of the polyester microstructure, meaning the degree of branching, and

thus thermal properties via the catalyst system is an attractive challenge. Another well known catalyst system for alkoxycarbonylation reactions comprises a palladium source and phosphine ligands. Triphenylphosphine **4** was studied, as corresponding Pd(II) catalysts are well known to promote alkoxycarbonylation of various olefins.[28, 81-83] In addition certain electron-rich bulky diphosphines (**1** to **3**, Scheme 3.3) were investigated. Other than diphosphines like 1,3-bis(di-phenylphosphino)propane, they favour alkoxycarbonylation over chain growth polymerisation to alternating polyketones.[38, 41, 86-87]



Scheme 3.3 Phosphine ligands with different electron density and steric hindrance.

Analysis of the reaction products of the palladium catalysed alkoxycarbonylation polymerisation of 10-undecen-1-ol employing the different phosphine ligands depicted in Scheme 3.3 using NMR spectroscopy revealed their influence on the reaction.

When utilising the dtbpx ligand **1** (Table 3.2, entries 1 and 2) only internal and thus isomerised olefins are present in the reaction mixture as well as oligomeric polyesters and many side products (Figure 3.4). This hints at a predomination of the isomerisation reaction over the insertion of carbon monoxide and the subsequent alcoholysis reaction of the thus resulting Pd-acyl species.

Alkoxycarbonylation of olefins using ligand **1** also results in the terminal, thus unbranched, ester product exclusively (entry 2) (cf. Figure A 4), even when applying internal olefins.[39] The bulkiness of the ligand, however, does not favour 1,2-insertion over 2,1-insertion as isomerisation predominates. It can be assumed that the steric hindrance of the phosphine

ligand **1** rather disables the formation of the branched palladium-acyl species or the alcoholysis reaction thereof.

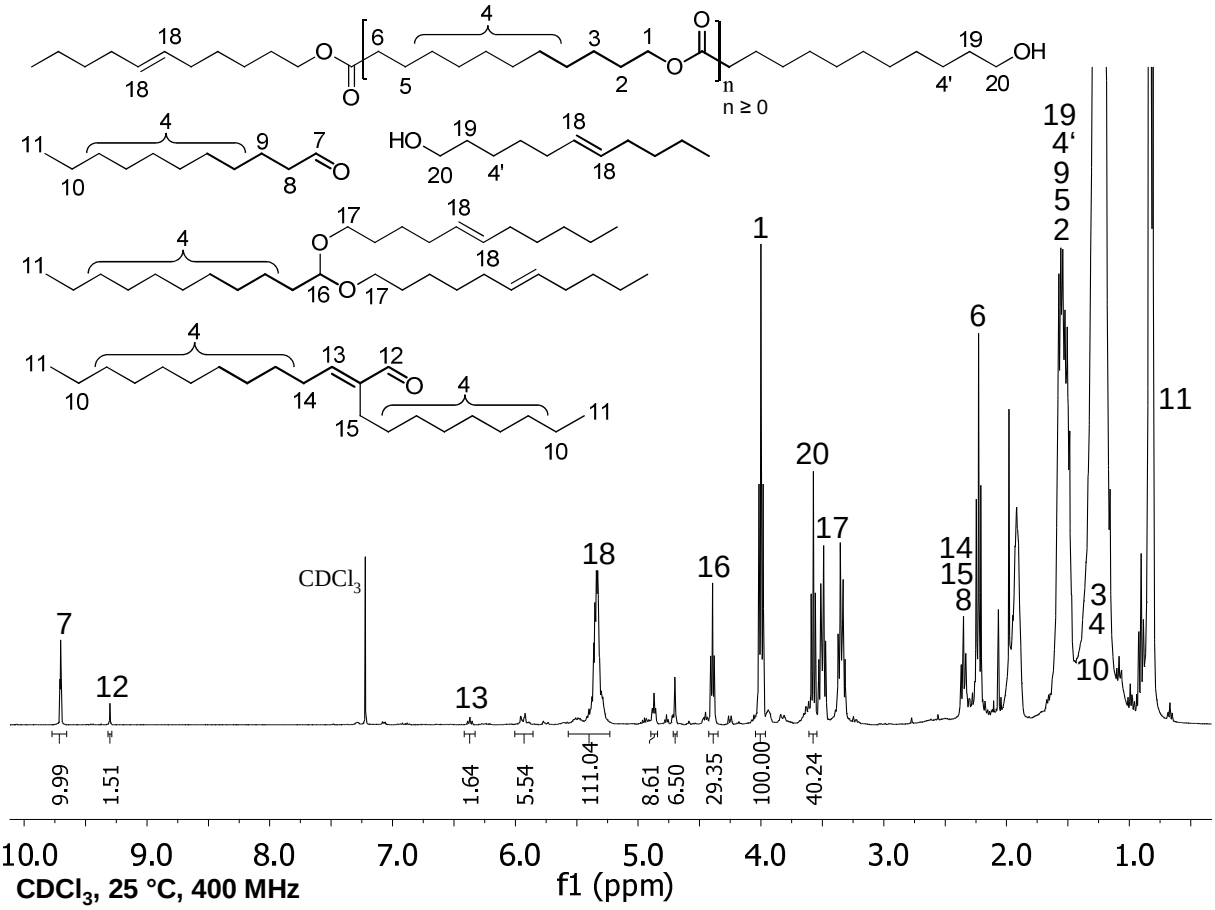
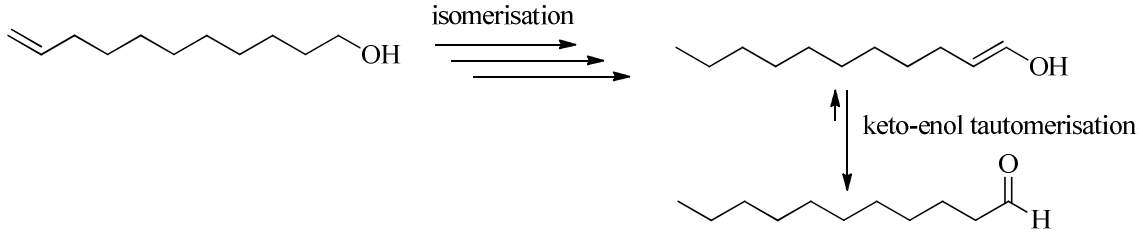


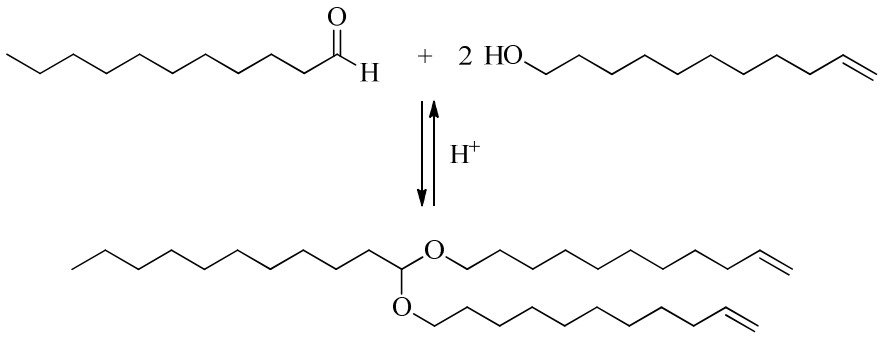
Figure 3.4 ^{1}H-NMR spectrum of the reaction mixture of the Pd(II)/dtbpx catalysed alkoxycarbonylation polymerisation of 10-undecen-1-ol (Table 3.2, entry 1).

The many side products originate from undecanal which in turn originates from the rapid isomerisation reaction leading to undec-1-en-1-ol which readily undergoes keto-enol tautomerisation (Scheme 3.4).[88]



Scheme 3.4 Formation of undecanal by isomerisation of 10-undecen-1-ol via repeated β-hydride elimination and subsequent keto-enol tautomerisation.

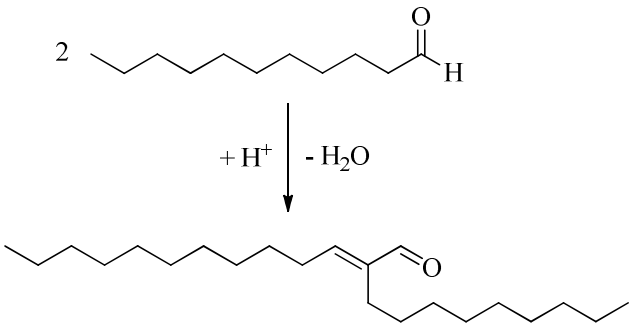
The thus formed undecanal can react with two further equivalents of 10-undecen-1-ol or the growing polymer chain to the corresponding acetal (Scheme 3.5). This reaction is detrimental for achieving high molecular weight polyesters as it violates the stoichiometry of the alkoxycarbonylation reaction. The acid catalysed acetal formation leads to the generation of two olefin end-groups and thus an excess thereof. In this way highly branched polyesters with limited molecular weights are formed. The higher degree of branching and the longer character of the branches is reflected by the lower melting temperature T_m = 62 °C of the small portion polymer obtained (entry 2).



Scheme 3.5 Acid catalysed acetal formation from undecanal and 10-undecen-1-ol.

The undecanal from the isomerisation of 10-undecen-1-ol can also undergo an aldol reaction (Scheme 3.6 and Figure 3.4), but the reaction product does not influence the alkoxycarbonylation reaction as it was only found and identified in the filtrates of the precipitated polymers by NMR spectroscopy.

When applying the dtbpp ligand **2** in the alkoxycarbonylation polymerisation of 10-undecen-1-ol higher conversions to the polyester product can be achieved (Table 3.2 entries 3-5). This is also evident from the smaller amount of side reactions, namely the isomerisation of the olefin resulting in undecanal and subsequent acetal formation.



Scheme 3.6 Aldol reaction of undecanal via the acid catalysed enol mechanism.

For this ligand the influence of the carbon monoxide pressure was studied. 50 bar appeared to be optimal as both higher pressure of 100 bars and lower pressure of 30 bar led to more side reactions, evident from higher yields in actal and less polymer. Interestingly the polyester obtained by reaction at 100 bar carbon monoxide exhibits a bimodal distribution of molecular weights according to GPC traces which hints at the formation of macrocycles.[89] All polyester products exhibit 3 to 7 % of mainly methyl branches next to the carbonyl of the ester moiety (cf. Figure 3.5).

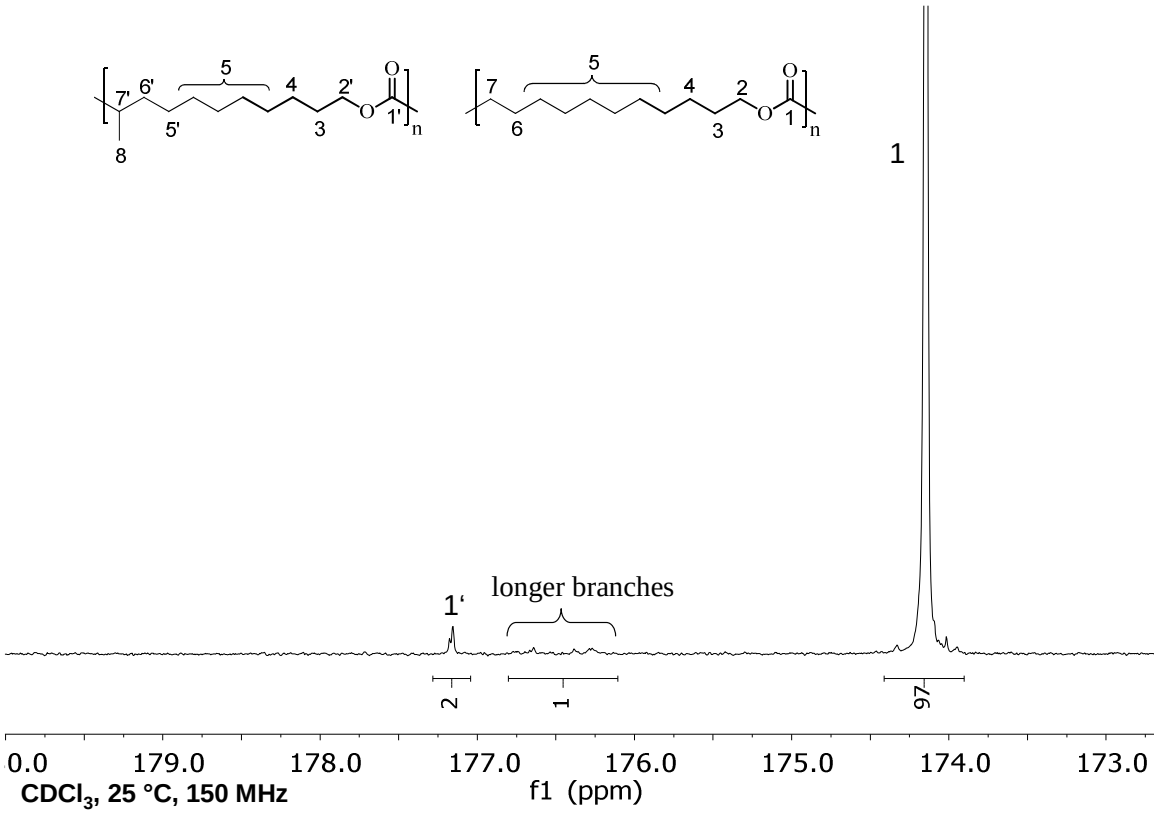


Figure 3.5 Carbonyl region of the $^{13}C\{^{1}H\}$-NMR spectrum of poly(dodecyloate) prepared with Pd(II)/dtbpp catalyst (Table 3.2, entry 4).

Again, the amount of acetal incorporated into the polymer chain and the branches generated in this way strongly influence its thermal properties. The polyester isolated from the reaction at 50 bar exhibited the highest melting temperature of T_m = 76 °C (Figure 3.6) with also the lowest degree of branching and the lowest amount of acetal moieties (entry 4).

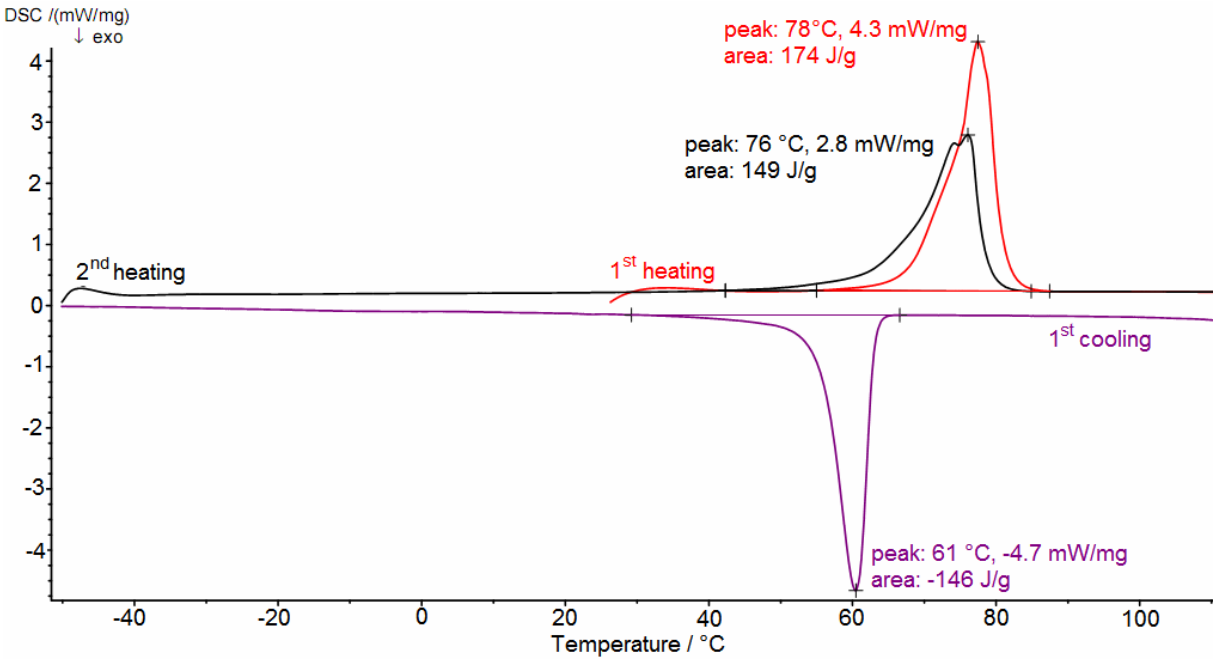


Figure 3.6 DSC trace of poly(dodecyloate) prepared with Pd(II)/dtbpp catalyst (Table 3.2, entry 4).

Ligand **3** leads to even higher conversions towards the polyester product, suggesting a decreased amount of isomerisation and thus side reactions (Table 3.2, entries 6-8). The obtained polyesters exhibit a similar degree of branching like the polyesters obtained with ligand **2**. Increase of the reaction time from 18 to 70 hours lead to a slight increase in the molecular weight of the isolated polyester product, which is however accompanied by an increased formation of acetal species. Surprisingly, this does not affect the thermal properties of the obtained polyesters which show melt peaks of around 70 °C (entries 6 and 7). Polyester with very similar molecular weight, degree of branching, amount of acetal and melting temperature was obtained with an increased reaction temperature of 125 °C, slightly lower carbon monoxide pressure of 40 bar and a reaction time of 5 hours (entry 8). The polymer yield however decreased by around 50 % compared to the other experiments.

Table 3.2 Polymerisation results of the Pd/phosphine ligand catalysed carbonylation polymerisation of 10-undecen-1-ol.

entry	ligand (P:Pd)	T / °C	P / bar	t / h	Polyester yield[a] / [g]	$M_w \times 10^3$ (GPC)[b] / g mol^{-1}	$M_n \times 10^3$ (GPC)[b] / g mol^{-1}	Integral[c] acetal 4.4 ppm	T_m / °C	degree of branching[d]
1	**1** (4.3)	90	50	18	n.d.[e]	n.d.	n.d.	29.4[f]	n.d.	n.d.
2	**1** (4.3)	70	50	48	0.05	1.8	1.2	16.6	62	0 %
3	**2** (4.3)	90	30	18	2	3.0	1.5	10.8	64 / 68	5 %
4	**2** (4.3)	90	50	18	2	4.2	3.2	0.1	76	3 %
5	**2** (4.3)	90	100	18	0.1	3.1[g]	2.0[g]	6.9	73	7 %
6	**3** (4.3)	90	50	70	6.6	5.0	4.0	2.9	71	6 %
7	**3** (4.3)	90	50	18	7.5	3.6	2.7	0.6	69	n.d.
8[h]	**3** (4.4)	125	40	5	3	4.0	3.0	1.1	71	3 %
9[i]	**4** (14.8)	90	50	18	4	25	17	0.3	67 / 74	18 %
10[i]	**4** (14.8)	125	50	18	12	28	17	0.5	58 / 66	32 %

Polymerisations were performed in a 250 mL stainless steel autoclave in 50 mL toluene with 0.14 mmol $Pd(OAc)_2$, 50 mmol 10-undecen-1-ol and 10 equivalents of CH_3SO_3H relative to $Pd(OAc)_2$. [a] determined by precipitation from diethylether. [b] in THF vs. polystyrene standards. [c] ^{1}H-NMR spectra of precipitated material, integral of signal at 4.0 is set to 100. [d] next to the carbonyl of the ester moiety, determined by integration of the corresponding ^{13}C-NMR shifts in the carbonyl region. [e] no precipitate. [f] ^{1}H-NMR of reaction mixture after solvent removal. [g] bimodal distribution. [h] 0.27 mmol $Pd(OAc)_2$, 100 mmol 10-undecen-1-ol. [i] experiment performed by Dr. Cécile Bouilhac with 0.54 mmol $Pd(OAc)_2$ and 100 mmol 10-undecen-1-ol.

The highest molecular weight polyesters and highest yields were obtained utilising PPh_3 **4** (Table 3.2, entries 9 and 10). Only minor amounts of acetal species were detected. The polyesters however exhibit the highest degree of predomintly methyl branches next to the carbonyl of the ester moiety. Contrasting catalysis with ligands **1**-**3**, the selectivity of the alkoxycarbonylation polymerisation is dependent on the reaction temperature. Conducting the reaction at 90 °C afforded polyester with 18 % of branched ester moieties and complex melt behaviour, exhibiting two melt peaks around 70 °C (entry 9). Conducting the reaction at 125 °C polyester with 32 % of branched ester moieties and two melt peaks at around 62 °C (Figure 3.8) was obtained (entry 10). The higher reaction temperature also led to a significant increase in polymer yield.

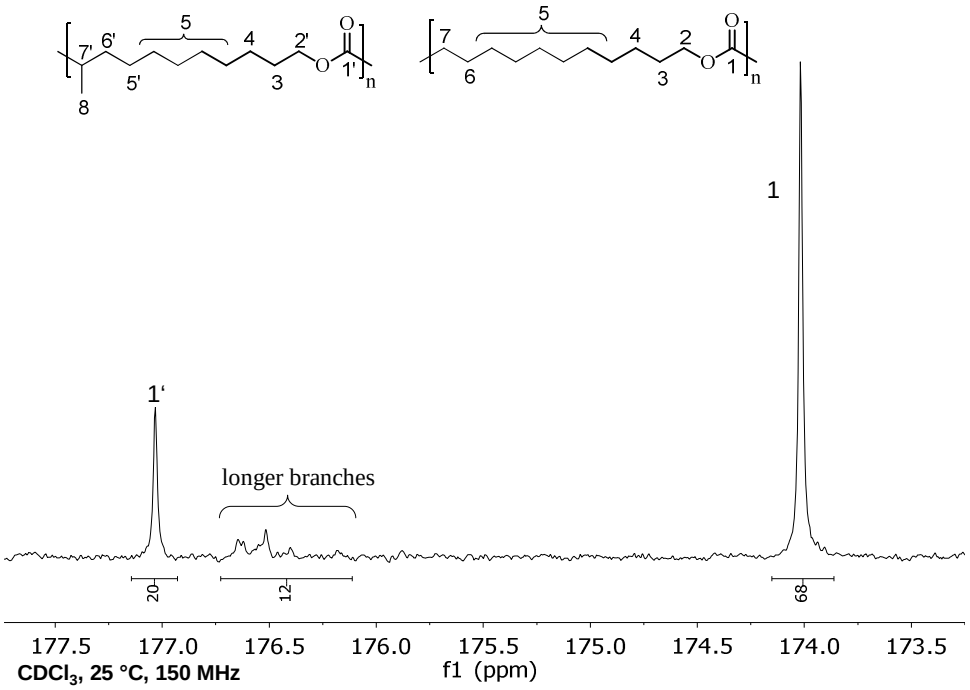


Figure 3.7 Carbonyl region of the $^{13}C\{^{1}H\}$-NMR spectrum of poly(dodecyloate) prepared with Pd(II)/PPh_3 catalyst (Table 3.2, entry 10).

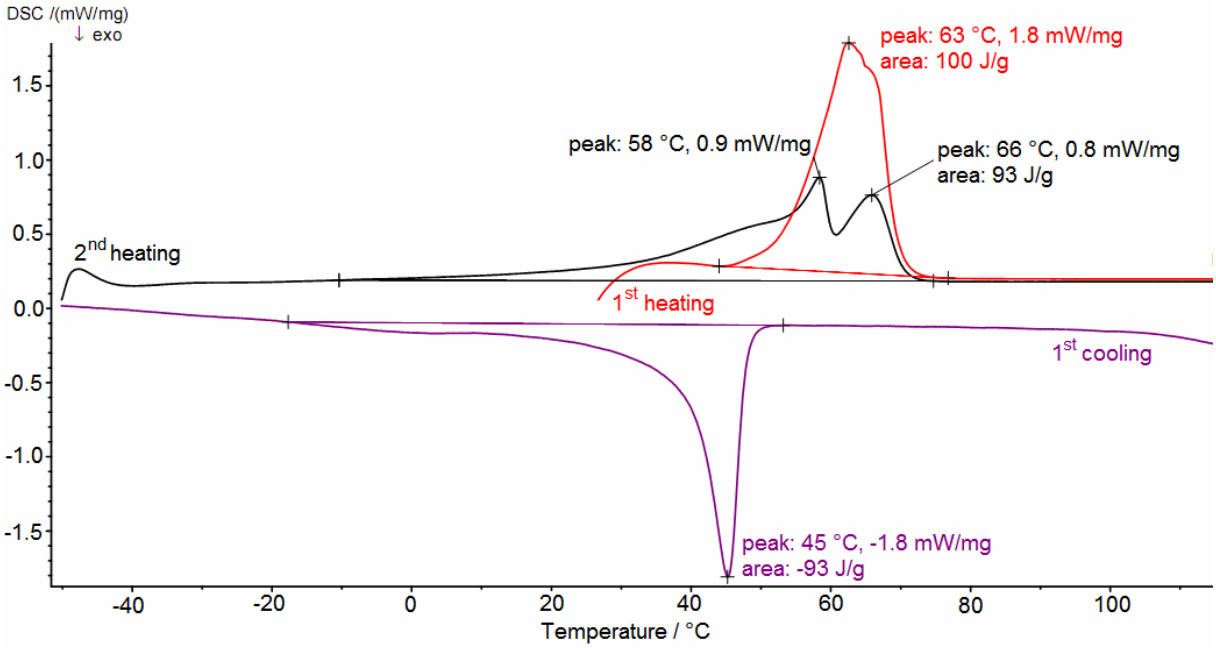
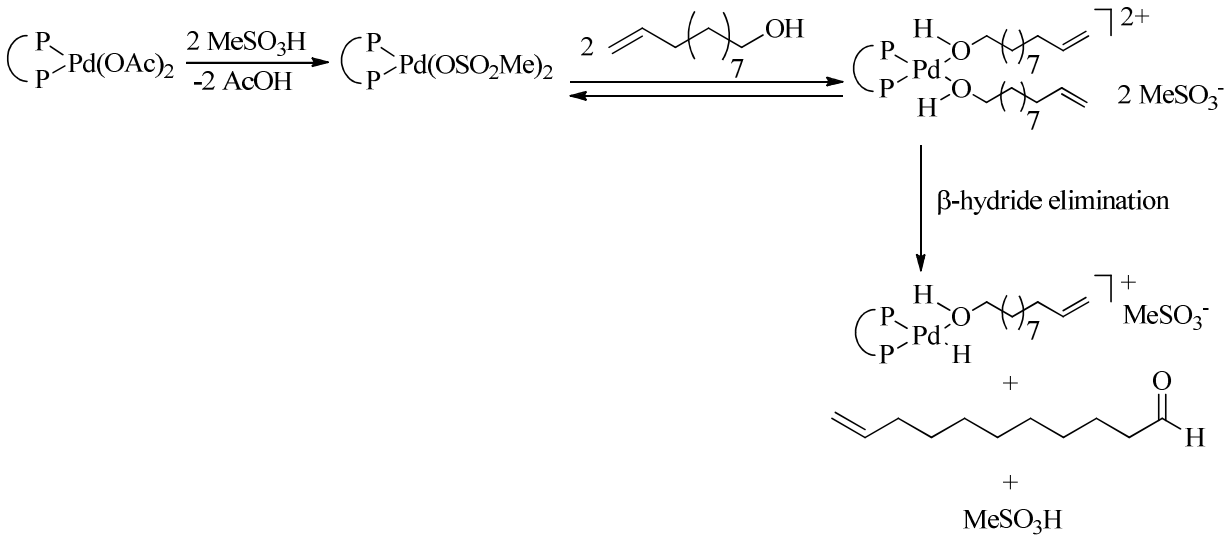


Figure 3.8 DSC trace of poly(dodecyloate) prepared with Pd(II)/PPh_3 catalyst (Table 3.2, entry 10).

In all the polymers isolated by precipitation of Table 3.2 at least traces of aldehyde end-groups were detected. These aldehyde end-groups are unreactive in alkoxycarbonylation

polymerisation and therefore limit the molecular weights of the resulting polyester. They are possibly formed by alkoxycarbonylation of undec-10-en-1-aldehyde, which is presumably produced by the formation of the initial palladium-hydride species. The catalyst precursor is palladium-acetate to which either a chelating diphosphine or two monodentate phosphins are coordinated. For catalyst activation these complexes react with two equivalents of a strong, non-coordinating acid, e.g. methanesulfonic acid, under liberation of acetic acid. It has been suggested [90-91] that the following coordination of alcohol and its subsequent β-hydride elimination lead to the formation of aldehyde species, which is unsaturated and thus reactive in alkoxycarbonylation in the case of 10-undecen-1-ol (Scheme 3.7).



Scheme 3.7 Possible activation pathway of in-situ catalyst under formation of undecenaldehyde.

In the alkoxycarbonylation reaction the reaction conditions strongly influence the occurrence of the isomerisation reaction. Ionescu et al.[88] attempted to synthesise lactones by ring-closing alkoxycarbonylation of 3-buten-1-ol, 3-buten-1-methyl-1-ol and 4-penten-1-ol in water. However, they primarily obtained the corresponding aldehydes in up to 98 % selectivity and no linear ester products. The phoshine ligands they applied were water soluble derivates of PPh_3, e.g. tppts, which are indeed less sterically demanding than phosphines **1**, **2**, and **3** (Scheme 3.3). Furthermore they worked with a ratio of acid to olefin of 0.7. This exceeds the amount of acid applied in the experiments of Table 3.2 by a factor of 25. It therefore seems that high amounts of acids and protic solvents promote the isomerisation reaction.

In summary, of the catalysts studied, both Pd(II) catalysts modified by triphenylphosphine **4** as well as the bulky, electron rich 1,3-bis(trioxa-adamantylphosphino)propane **3** convert the largest part of the 10-undecen-1-ol starting material to polyester. Molecular weights are highest for the PPh_3-modified catalyst. Nonetheless, branching of these materials results in slightly lower melting temperatures vs. the linear materials obtained with the bulky diphosphines **1** and **2**.

By comparison, a linear poly(dodecyloate) prepared by polycondensation from 12-hydroxydodecanoic acid with M_n = 63 × 10^3 g mol^{-1} (M_w/M_n = 2), as determined by GPC measurements in THF at 40 °C versus polystyrene standards, was found to posess a peak melting point of T_m = 87 °C (Figure 3.9). That is, the thermal properties of the polyesters from 10-undecen-1-ol carbonylation with **2** or **3** are influenced to some extent by the lower molecular weight and/or the small number of branches.

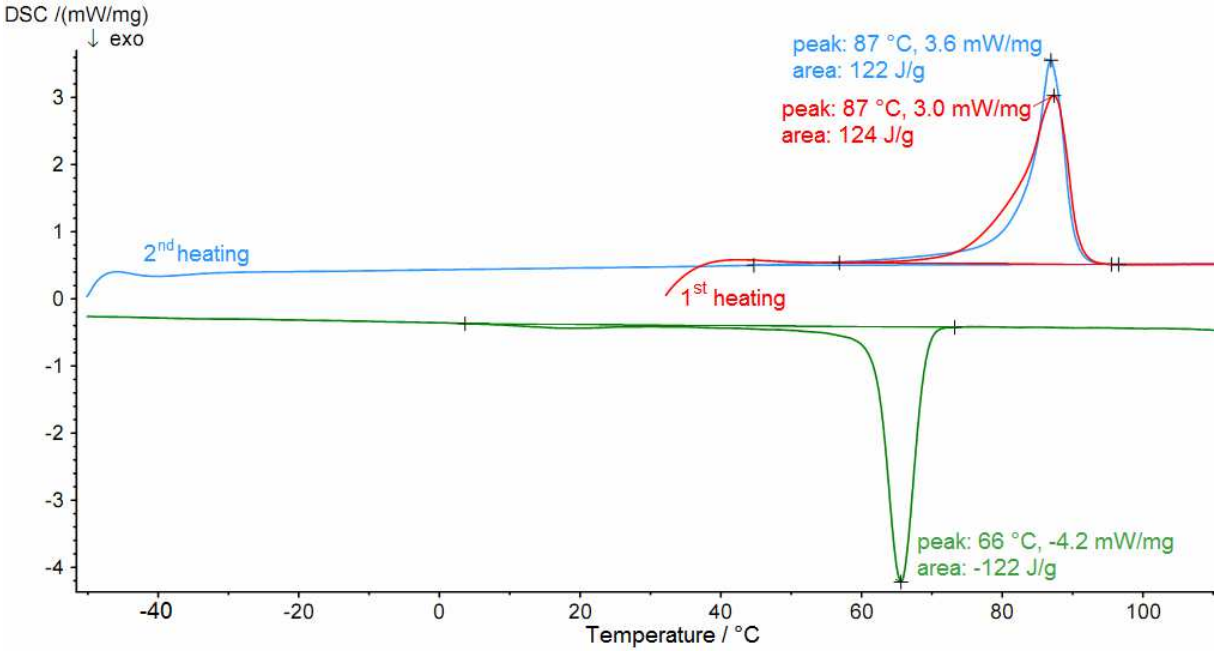


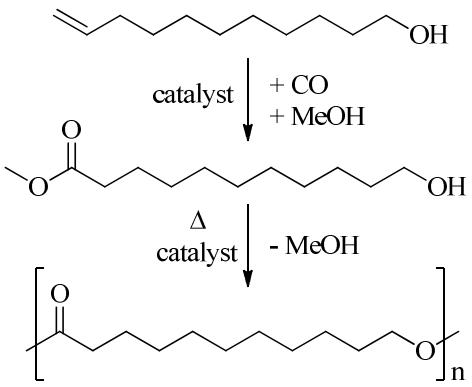
Figure 3.9 DSC trace of poly(dodecyloate) obtained by polycondensation of 12-hydroxydodecanoic acid, for comparison.

4 Poly(dodecyloate) from Methyl-12-hydroxydodecanoate

As illustrated above poly(dodecyloate) can be obtained directly in high molecular weights either by cobaltcarbonyl/pyridine catalysed or by palladium/PPh_3 catalysed alkoxycarbonylation polymerisation of 10-undecen-1-ol. A limitation of these two routes is,

that the material obtained is not entirely linear but exhibits around 20-35 % methyl- and longer branches. Branching is detrimental for thermal properties by leading to lower melt and crystallisation temperatures as expected for the entirely linear material. Therefore, an alternative route leading to linear poly(dodecyloate) from plant oil based 10-undecen-1-ol is desirable.

According to previous reports palladium catalysed alkoxycarbonylation of olefins, under formation of esters is the faster the smaller and the less sterically hindered the reacting alcohol.[36-37, 92] The resting state of the reaction is presumed to be a Pd-acyl complex, while the attack of alcohol at the Pd-acyl, the so-called alcoholysis, is considered to be the rate determining step.[37] As 10-undecen-1-ol is a rather large, and the hydroxyl-terminated growing polymer chain an even larger and sterically hindered alcohol, their nucleophilic attack in the alkoxycarbonylation polymerisation at the Pd-acyl is presumably comparatively slow. Depending on the choice of phosphine ligand the reaction is capable of providing highly linear polyester products (Table 3.2) however only with very limited molecular weights and a whole range of undesired side products originating from the competing isomerisation of the olefin. For achieving high molecular weight linear polymers the alcoholysis reaction should be accelerated. Faster alcoholysis could be achieved by utilising methanol as a nucleophile forming methyl-12-hydroxydodecanoate from 10-undecen-1-ol. In a subsequent polyesterification reaction the linear methyl-12-hydroxydodecanoate could then be converted into linear poly(dodecyloate) (Scheme 4.1).



Scheme 4.1 Poly(dodecyloat) by methoxycarbonylation of 10-undecen-1-ol and subsequent polyesterification.

4.1 Methyl-12-hydroxydodecanoate by Palladium-catalysed Methoxycarbonylation of 10-Undecen-1-ol

From the experiments illustrated in Table 3.2 the dtbpp ligand is supposed to be the most promising candidate for the palladium-catalysed methoxycarbonylation of 10-undecen-1-ol to form the linear methyl-12-hydroxydodecanoate selectively, as the most linear material could be obtained with only small amounts of side products using this ligand in 10-undecen-1-ol alkoxycarbonylation polymerisation (entries 3-5). In the range of temperatures and pressures studied, the optimum conditions for the alkoxycarbonylation polymerisation of 10-undecen-1-ol appeared to be 50 bar carbon monoxide pressure at 90 °C. Surprisingly, the reaction afforded the desired methyl-12-hydroxydodecanoate in only low yields of 30 % maximum (Table 4.1).

Table 4.1 Pd/dtbpp catalysed methoxycarbonylation of 10-undecen-1-ol.

entry	$Pd(OAc)_2$ / mmol	dtbpp / mmol	$MeSO_3H$ / mmol	methanol / mL	undecenol / mmol	t / h	undecenol / %	undecanal / %	acetal[a] / %	yield[b] / %
1[c]	0.14	0.3	0.25	45	50	22.5	-	2	74 %	24 %
2[d,e]	0.027	0.06	0.1	2	10	18	11[f]	2	58 %[g]	29 %
3[d]	0.027	0.06	0.05	1	10	15.5	58[h]	5	19 %[g]	18 %[i]

Methoxycarbonylations were performed at 90 °C and 50 bar carbon monoxide. [a] 1,1-dimethoxyundecane estimated from NMR. [b] yield of methyl-12-hydroxydodecanoate in the crude reaction mixture estimated from NMR. [c] in a 250 mL stainless steel autoclave. [d] in a 20 mL stainless steel autoclave. [e] addition of 2 mL toluene as solvent. [f] isomerised undecenol. [g] approx. 20 % undecoxyundecane. [h] approx. 30 % not isomerised undecenol. [g] approx 50 % undecoxyundecane. [i] 3 % α-methoxy-ω-hydroxydodecyloate.

When working with a large excess of methanol, the major product is 1,1-dimethoxyundecane (entry 1), which is formed by acid catalysed acetalisation reaction of undecanal with methanol (Scheme 3.5). 2 to 4 % of unreacted undecanal were detected in the reaction mixture. Undecanal is formed by isomerisation of 10-undecen-1-ol via repeated β-hydride elimination steps and final keto-enol tautomerisation (Scheme 3.4). Under these conditions the isomerisation is assumed to be much faster than the alkoxycarbonylation, meaning the Pd-acyl formation and the nucleophilic attack of methanol in particular, as relatively large amounts of undecanal and hence acetal are formed. Reduction of the amount of alcohol and addition of toluene as solvent (entry 2) seems to reduce the isomerisation reaction as the yield of the desired methyl-12-hydroxydodecanoate increased. Due to the reduced concentration of methanol minor amounts (2 %) of α-methoxy-ω-hydroxydodecyloate (Scheme 4.3) were formed by nucleophilic attack of 10-undecen-1-ol at Pd-12-hydroxydodecanacyl. No other

side reactions and thus side products appeared. Moreover, 10 % of isomerised, but for methoxycarbonylation reactive undecenol, were present. When reducing the amount of methanol even more but without adding toluene as solvent (entry 3) the isomerisation reaction can be further slowed down. This is evident from the equal amounts of acetal and methyl-12-hydroxydodecanoate detected in the reaction mixture by NMR spectroscopy. However, not only 1,1-dimethoxyundecane is formed but also any possible other acetal from 10-undecen-1-ol and methanol (Figure 4.1).

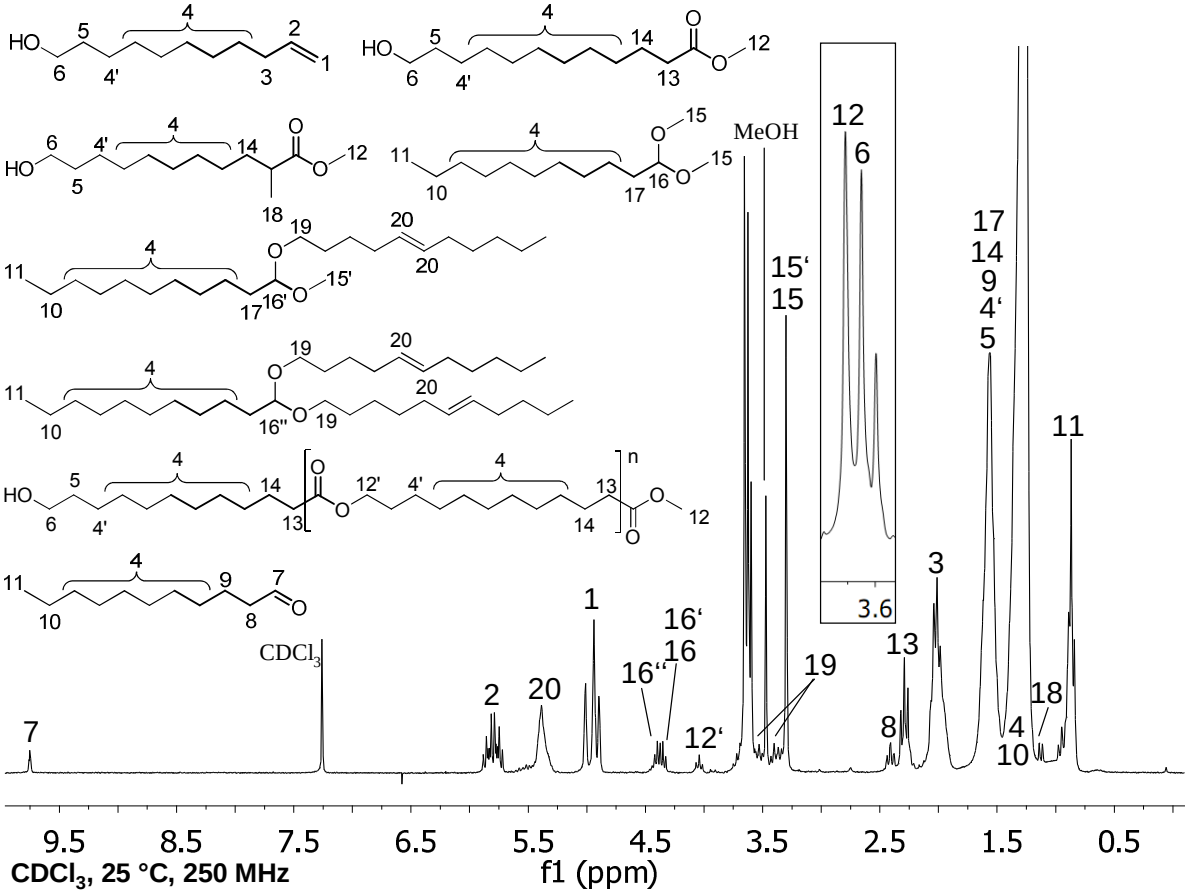


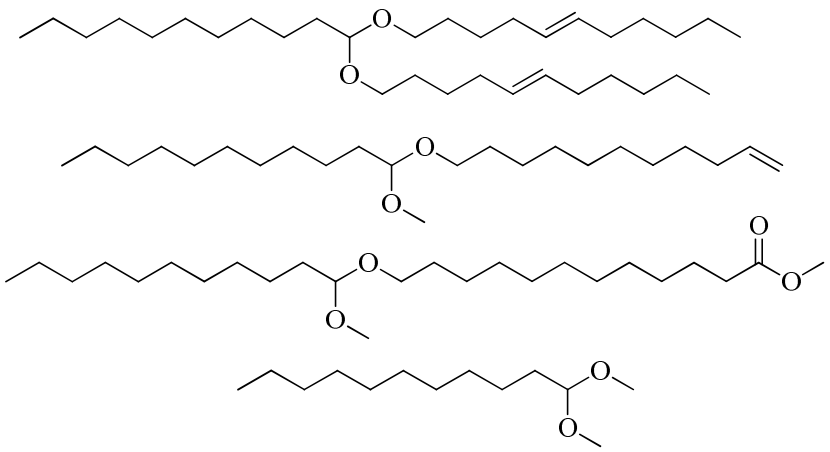
Figure 4.1 ^{1}H-NMR spectrum of the methoxycarbonylation of 10-undecen-1-ol with the dtbpp ligand (**Table 4.1**, entry 3).

The lower methanol content not only reduces the isomerisation reaction but also leads to lower catalyst activity as approximately 30 % unreacted 10-undecen-1-ol are present and product yields of only 18 % were obtained. Other than expected the dtbpp ligand does not yield the entirely linear methyl-12-hydroxydodecanoate but also produces traces of the methyl branched product (Figure 4.1). In case of the dtbpp ligand suppression of the isomerisation reaction by adjusting the reaction conditions is not possible which makes this ligand less

suitable for the methoxycarbonylation of 10-undecen-1-ol to form methyl-12-hydroxydodecanoate as monomer for linear poly(dodecyloate).

The dtbpx ligand is the most reactive ligand in the methoxycarbonylation of ethylene. Therefore it should form a suitable catalyst system with palladiumacetate and methanesulfonic acid in the methoxycarbonylation of 10-undecen-1-ol. Moreover it is expected to form the linear methyl-12-hydroxydodecanoate exclusively.

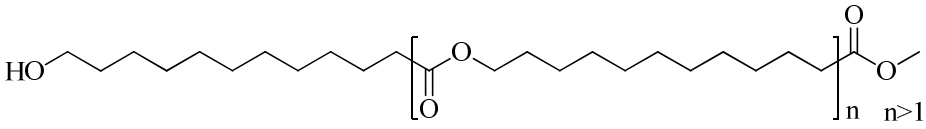
According to Jiménez-Rodriguez et al. highly selective formation of linear esters can be achieved by methoxycarbonylation of terminal alkenes catalysed by palladium complexes of dtbpx formed in situ from $Pd(dba)_2$, excess ligand and methanesulfonic acid. Selectivity and conversion are supposedly highest when exposing the reaction mixture to carbon monoxide at ambient temperature.[39] Applying these literature conditions to the methoxycarbonylation of undec-10-1-ol leads to very low yields of methyl-12-hydroxydodecanoate of only 4 % (Table 4.2, entry 1). Again the isomerisation reaction dominates the methoxycarbonylation leading to a whole range of side products all arising from the aldehyde formed by repeated β-hydride elimination and subsequent keto-enol tautomerisation. Not only the 1,1-dimethoxyundecane is formed but also different acetals from undecenol or methyl-12-hydroxydodecanoate (Scheme 4.2). Furthermore, approximately 4 % of acid catalysed aldol reaction products (Scheme 3.6) were detected in the reaction mixture. (For a detailed NMR analysis of the product mixture see Figure A 5,Figure A 6 and Figure A 7).



Scheme 4.2 Some possible acetals in the reaction mixture (Table 4.2, entry 1).

The reaction conditions under which the highest yield of methyl-12-hydroxydodecanoate was obtained with the dtbpp ligand (Table 4.1, entry 2) did not lead to high yields when using the dtbpx ligand (Table 4.2, entry 3). With the dtbpx ligand isomerisation is even more dominant

than with the dtbpp ligand although the yield could be slightly hampered by the higher amount of methanesulfonic acid applied which catalyses side reactions. Nevertheless, with 4 % the yield is much lower than with the dtbpp ligand with even higher amounts of acid (Table 4.1, entry 1). The highest yield of methyl-12-hydroxydodecanoate utilising the dtbpx ligand was obtained at 90 °C under 50 bar carbon monoxide pressure with two equivalents of methanesulfonic acid relative to palladium acetate and a ratio of undec-10-1-ol to methanol of 1 to 2.5 (Table 4.2, entry 4). Under these conditions considerable amounts (~20 %) of oligomers (Scheme 4.3) were formed, due to the rather low amount of methanol. In contrast to earlier reported findings, in this case the nucleophilic attack of the long 10-undecen-1-ol seems to be favoured over the nucleophilic attack of methanol. However, when replacing methanol with ethanol (Table 3.1, entry 2), catalyst activity is reduced and thus isomerisation and alkoxycarbonylation. Only 12 % of the ethyl-12-hydroxydodecanoate and around 60 % of isomerised undecenol were obtained.



Scheme 4.3 Oligomers formed during methoxycarbonylation of 10-undecen-1-ol.

As the melting temperature of methyl-12-hydroxydodecanoate is 31 °C,[93] the reaction mixture was cooled to approximately 4 °C to separate the desired product via crystallisation. Due to acetal formation traces of water are present in the reaction mixture, which results in the equilibrium formation of aldehyde hydrates.[94-95] Unfortunately, the formation of the hydrates is favoured at lower temperatures and the aliphatic ones comprising more than seven carbon atoms are solids at RT.[96] Therefore it was not possible to obtain the pure methyl-12-hydroxydodecanoate by crystallisation as the aldehyde hydrates coprecipitated.

Distillation of the reaction mixture was not possible as the boiling point of 1,1-dimethoxyundecane is at 105-108 °C at 3 Torr[97], the boiling point of undecanal at 98-100 °C at 3 Torr and the boiling point of methyl-12-hydroxydodecanoate is expected to be even higher. Separation by distillation of substances showing boiling points of higher 100 °C with a boiling point difference smaller than 20 °C at pressures lower than 10 mbar is generally difficult. Furthermore the distillation conditions already resemble polymerisation conditions. However, direct polymerisation of the crude reaction mixture under simultaneous removal of

the side products is not recommendable as there might be acetal species with one or two ester moieties present (cf. Scheme 4.2) which either represent monofunctional monomers and thus yield unreactive chain ends or would lead to highly branched material.

Table 4.2 Palladium catalysed methoxycarbonylation of 10-undecen-1-ol with dtbpx as a ligand.

entry	$Pd(OAc)_2$ / mmol	dtbpx / mmol	$MeSO_3H$ / mmol	methanol / mL	undecenol / mmol	t / h	undecanal / %	acetal / %	yield[a] / %
1[b]	0.13[c]	0.39	1.3	10	10	3	13	79	4
2	0.08	0.18	0.15	4.5[d]	30	18	1	15	13[e]
3[f]	0.027	0.06	0.25	2	10	19.5	6	90	4
4	0.027	0.06	0.05	1	10	23	4	63	34[g]

Methoxycarbonylations were performed in a 20 mL stainless steel autoclave at 90 °C and 20 bar carbon monoxide. [a] yield of methyl-12-hydroxydodecanoate in crude reaction mixture determined by NMR. [b] in a 15 mL Schlenk at RT, carbon monoxide was admitted to the reaction mixture at 1 bar. [c] $Pd(dba)_2$. [d] ethanol. [e] ethyl-12-hydroxydodecanoate [f] addition of 4 mL toluene as solvent. [g] 14 % methyl-12-hydroxydodecanoate and 20 % α-methoxy-ω-hydroxydodecyloate.

From the experiments in Table 4.1 and Table 4.2 it has to be concluded that the palladium/phosphine ligand in situ catalyst system, in combination with either the dtbpp or dtbpx ligand, is not suitable for the formation of methyl-12-hydroxydodecanoate via methoxycarbonylation of 10-undecen-1-ol although these two ligands are well-known to form the linear ester products exclusively in the alkoxycarbonylation of either terminal or internal olefins. In contrast to ω-hydroxy functionalised 1-olefins the isomerisation of the double bond in unsubstituted olefins does not represent a major issue. It is also not possible to suppress the isomerisation reaction by adjusting the reaction conditions. Interestingly, the isomerisation reaction occurs to a considerably higher extent in the presence of methanol and therefore severely hampers the formation of Pd-acyl species and the subsequent nucleophilic attack of alcohol and thus the alkoxycarbonylation reaction. The aldehyde formation, as a result of the isomerisation reaction, and further side products thereof severely limit the yields of the desired methyl-12-hydroxydodecanoate. The isolation of the product proves to be highly difficult and would have to involve column chromatography which is undesirable for larger scales and of course industrial application.

4.2 Methyl-12-hydroxydodecanoate by Cobalt-catalysed Methoxycarbonylation of 10-Undecen-1-ol

As illustrated in Table 3.1 the cobalt-catalysed alkoxycarbonylation of 10-undecen-1-ol leads to high molecular weight polyesters with negligible amounts of side products. Nevertheless, the ^{1}H-NMR spectrum of the thus obtained poly(dodecyloate) (Figure 3.2) reveals the presence of residual and still reactive internal olefin and alcohol end-groups. Other than in the palladium-catalysed alkoxycarbonylation the isomerisation reaction of the olefin occurs to a considerably smaller extent than the ester formation through an acyl-cobalt species and the subsequent alcoholysis reaction. However, the presence of unreacted olefin and alcohol end groups suggests that in its later stages the alkoxycarbonylation polymerisation is very slow, possibly due to the low concentration of two of the functional groups required. Complete conversion therefore seems to be difficult to achieve and thus the polymer molecular weights obtained via cobalt catalysed alkoxycarbonylation polymerisation of 10-undecen-1-ol remain limited as the reaction follows a step growth mechanism.

Similar as in palladium-catalysed alkoxycarbonylation of olefins, the rate determining step in cobalt-catalysed alkoxycarbonylation is considered to be the alcoholysis of the acyltetracobaltcarbonyl complex.[51] It has been shown that in cobalt-catalysed alkoxycarbonylation the alcoholysis reaction is the fastest when utilising ethanol also leading to the highest yields of up to 99 % of desired ester with a linearity of greater 80 %.[84] Combining these very high yields and the increased linearity in ester formation with the possibility of achieving higher conversions of functional groups in a condensation reaction thus leading to higher molecular weight polyesters, makes the route to poly(dodecyloate) going over the methyl- or ethyl-12-hydroxydodecanoate highly attractive.

Alkoxycabonylation of 10-undecen-1-ol was investigated utilising either methanol or ethanol. In terms of functional group conversion ethanol seems to be slightly advantageous over methanol (Table 4.3 entries 1 and 2 versus 3 and 4). 100 % conversion of the 10-undecen-1-ol was achieved by increasing the reaction time (entry 4). The alcohol concentration has considerable influence on the reaction. With a ten-fold excess of methanol over 10-undecen-1-ol (Table 4.3, entry 1) the lowest yield of 62 % was obtained. By reducing the alcohol concentration to a five-fold excess alcohol over 10-undecen-1-ol the yield increased to 74 % (entry 2).

Table 4.3 Cobalt catalysed methoxycarbonylation of 10-undecen-1-ol.

entry	10-undecen-1-ol / mmol	methanol / mL	t / h	unreacted double bond / %	oligomers / %	degree of branching[e] / %	yield[a] / %
1	75	30	17.5	24 %	14	13 %	62
2	150	30	18	14 %	12	20 %	74
3	150	44[b]	68	1 %	21	18 %	78[c]
4[d]	150	44[b]	115	0 %	24	16 %	76[c]

Methoxycarbonylations were performed in a 280 mL stainless steel autoclave at 160 °C, a starting pressure of 160 bar carbon monoxide, an 10-undecen-1-ol to $Co_2(CO)_8$ ratio of 75 and a pyridine to Co ratio of 32. [a] yield of methyl-12-hydroxydodecanoate in crude reaction mixture determined by NMR. [b] ethanol. [c] ethyl-12-hydroxydodecanoate. [d] 130 bar starting pressure. [e] calculated from carbonyl signals in ^{13}C-NMR spectra.

Interestingly, the amount of oligomers formed, originating from alkoxycarbonylation involving the hydroxyl functionality of 10-undecen-1-ol, did not increase by reducing the amount of alcohol applied. However, when replacing methanol with ethanol the amount of oligomer formed increased indeed (entry 3). In general, the cobalt-catalysed alkoxycarbonylation did not produce any undesired side products, as is the case for palladium-catalysed alkoxycarbonylation (cf. sections 3.2 and 4.1).

In summary, the cobalt-catalysed transformation of the olefin functionality in 10-undecen-1-ol to form a 12-hydroxydodecanoic acid ester lead to highest yields when applying ethanol in a five-fold excess over 10-undecen-1-ol at a reaction time of 115 hours. This approach led to a monomer readily applicable for polycondensation (cf. Figure 4.2, Figure A 11 and Figure A 12) after removal of cobalt catalyst residues by extraction of a dichloromethane solution with acidic aqueous EDTA solution in the presence of hydrogen peroxide. However, the thus obtained monomer also comprises around 20 % of branched product, which, after polycondensation, will lead to poly(dodecyloate) with a degree of branching of 20 % similar to the poly(dodecyloate) from direct alkoxycarbonylation polymerisation of 10-undecen-1-ol (section 3.1).

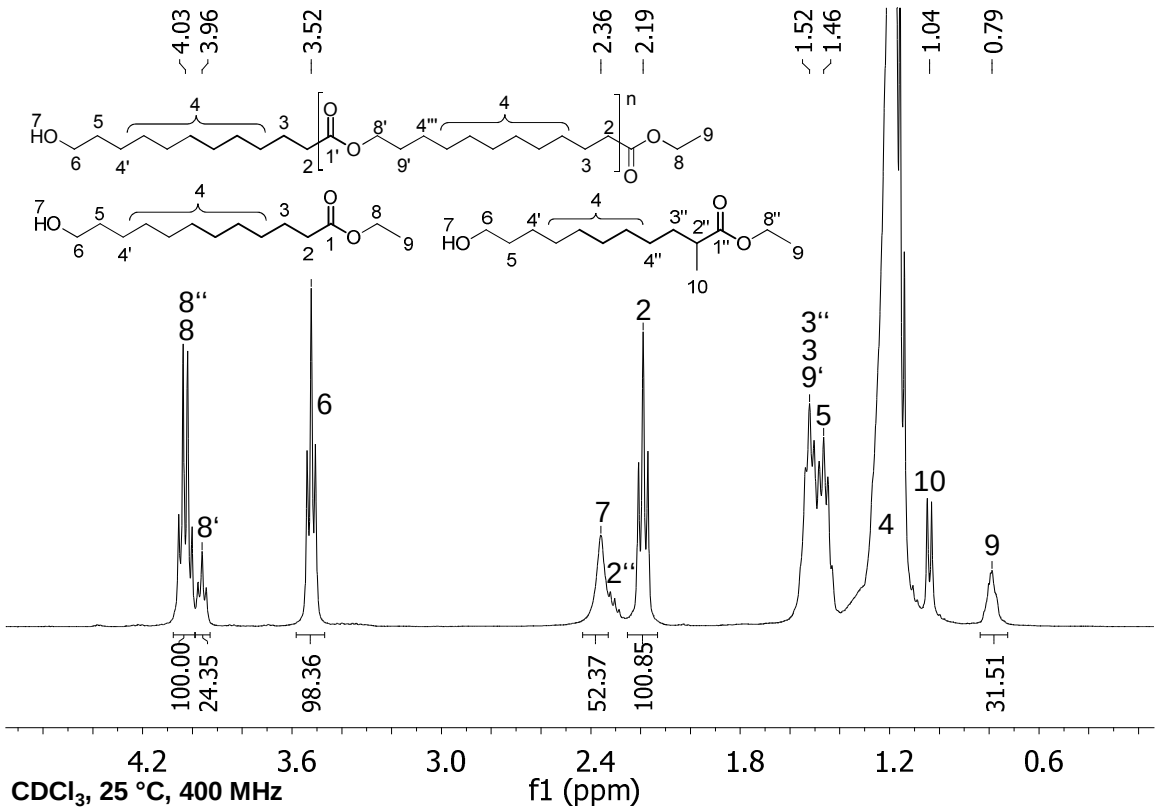


Figure 4.2 ^{1}H-NMR spectrum of crude ethyl-12-hydroxydodecanoate (Table 4.3, entry 4).

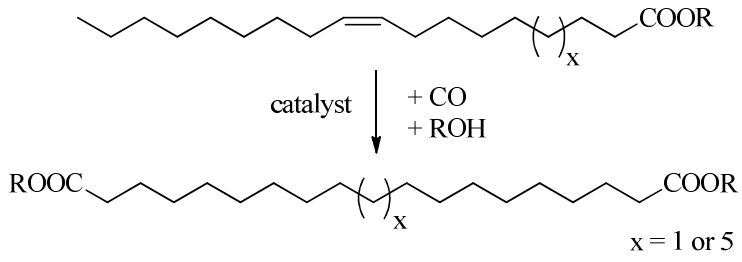
4.3 Polycondensation of Methyl- and Ethyl-12-hydroxydodecanoate

The methyl- and ethyl-12-hydroxydodecanoates obtained via cobaltcarbonyl/pyridine catalysed alkoxycarbonylation of 10-undecen-1-ol were converted to poly(dodecyloate) in a polycondensation reaction of a transesterification manner under elimination of methanol or ethanol respectively (Scheme 4.1). After removing residual cobalt catalyst from the reaction mixtures the thus obtained methyl- and ethyl-12-hydroxydodecanoates were utilised in the transesterification polymerisation without any further purification. $Ti(OBu)_4$ and $Ti(O^iPr)_4$ served as catalysts both providing poly(dodecyloate) of comparable molecular weights. The methyl-12-hydroxydodecanoate (entry 2, Table 4.3) with $Ti(O^iPr)_4$ as catalyst yielded poly(dodecyloate) with $M_w = 10 \times 10^3$ g mol^{-1} ($M_w/M_n = 2$) according to GPC (in THF at 50 °C vs. polystyrene standards), T_m = 65 °C and T_c = 50 °C. The ethyl-12-hydroxydodecanoate (entry 4, Table 4.3) with $Ti(OBu)_4$ as catalyst yielded poly(dodecyloate) with $M_w = 15 \times 10^3$ g mol^{-1} ($M_w/M_n = 2$), T_m = 61 °C and T_c = 48°C with a degree of branching of around 20 % (Figure A 13), reflecting the relative amount of branched monomer applied in the reaction.

In summary, the direct alkoxycarbonylation polymerisation of undec-10-1-ol is not only the more direct route to poly(dodecyloate) it also leads to polyesters of approximately the same molecular weights and degrees of branching as the route going over the methyl- or ethyl-12-hydroxydodecanoate (also cf. section 3).

5 Linear Semicrystalline Polyesters from Methyl Oleate and Ethyl Erucate

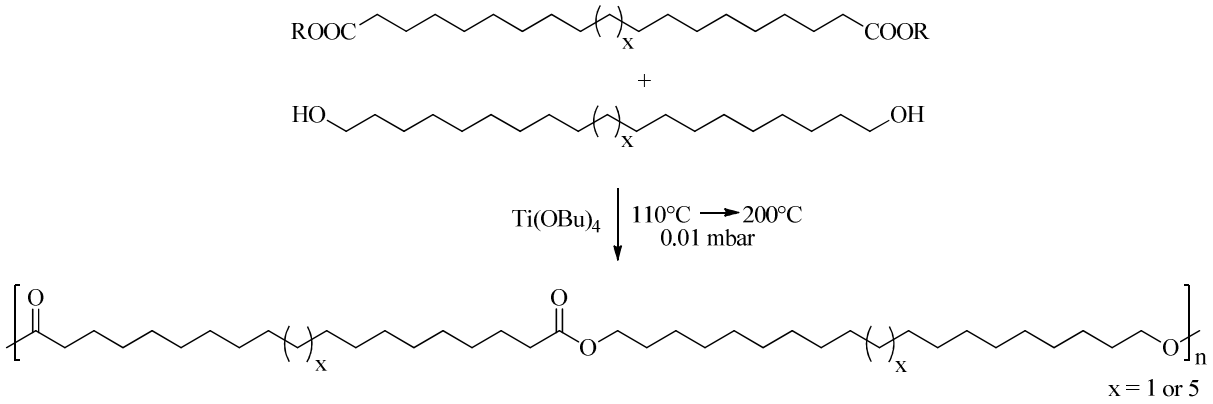
With the synthesis of poly(dodecyloate) it was already possible to obtain a polymer from renewable resources via an entirely chemical catalytic route. Unfortunately in this approach only one side of the fatty acid chain with respect to the double bond is incorporated into the monomer and ultimately the polymer. Also the material suffers from melting points insufficient for thermoplastic applications. But polymer production from a renewable resource ideally allows for a complete molecular utilisation of the feedstock and carries its molecular structure over into the resulting polymers, providing them with specific desirable properties. In this regard the complete molecule utilisation of fatty acids from plant oils is attractive as they already contain long chain linear crystallisable segments which could provide melt- and crystallisation temperatures suitable for thermoplastics. Unsaturated plant oils possess two functional groups, as required in principle for the generation of thermoplastics by step-growth polymerisation. However, the double bond is located in the centre of the molecule. For complete utilisation of fatty acids in the generation of crystallisable linear polymers, a functionalisation at the chain end is required (Scheme 1.1).



Scheme 5.1 Isomerising alkoxycarbonylation of unsaturated fatty acid esters yielding α,ω-diesters.

An efficient and highly regio- as well as chemoselective conversion of an internal double bond to a terminal functional group is a challenge for synthetic chemistry. To this end, palladium(II) complexes of very bulky substituted electron rich diphosphines catalyse the reaction of ethylene with carbon monoxide and methanol to methylpropionate (methoxycarbonylation) at high rates.[29, 98] Remarkably in the context of the present work,

these catalyst systems also methoxycarbonylate internal octenes to the linear carboxylic acid methyl esters.[38] They have been briefly noted to be compatible with unsaturated fatty acids (Scheme 5.1). From the gas chromatographic data of the reaction mixture presented, it appears however, that the carbonylation products were not formed or isolated with a purity sufficient for utilisation as a difunctional monomer for polycondensation.[99-100] This is critical as highly pure monomers are a prerequisite for achieving any substantial molecular weights in subsequent polycondensation reactions (Scheme 5.2).



Scheme 5.2 Polyesterification of plant oil based α,ω-diesters and α,ω-diols to long-chain aliphatic polyesters.

Possible unsaturated fatty acid esters for realising this concept are oleic acid esters with their 18 carbon atom aliphatic chain and erucic acid esters with their 22 carbon atom chain. Oleic acid esters are accessible from either high oleic sunflower oil or rape seed oil, erucic acid esters also from certain rape seed oils and crambe.

5.1 Isomerising Methoxycarbonylation of Methyl Oleate

Jiménez-Rodriguez et al. describe the isomerising methoxycarbonylation of methyl oleate utilising 1.6 mol-% palladium with a five-fold excess of dtbpx ligand and a ten-fold excess of methanesulfonic acid as in situ catalyst system and the analysis of the crude reaction mixture by gas chromatography. The reaction is conducted for 22 hours at 40 °C, 20 bar carbon monoxide pressure with a 41-fold excess of methanol relative to methyl oleate.[99]

An experiment conducted under optimised conditions in our lab yielded 76 % of dimethyl-1,19-nonadecanedioate (Table 5.1, entry 1). Isolation of the very pure product was achieved by crystallisation from the reaction mixture. The very high purity of greater 99 % obtained in this way was revealed by gas chromatography (Figure A 14) and ^{1}H-NMR spectroscopy

(Figure 5.1). The complete linearity was further confirmed by ^{13}C-NMR spectroscopy (Figure A 15).

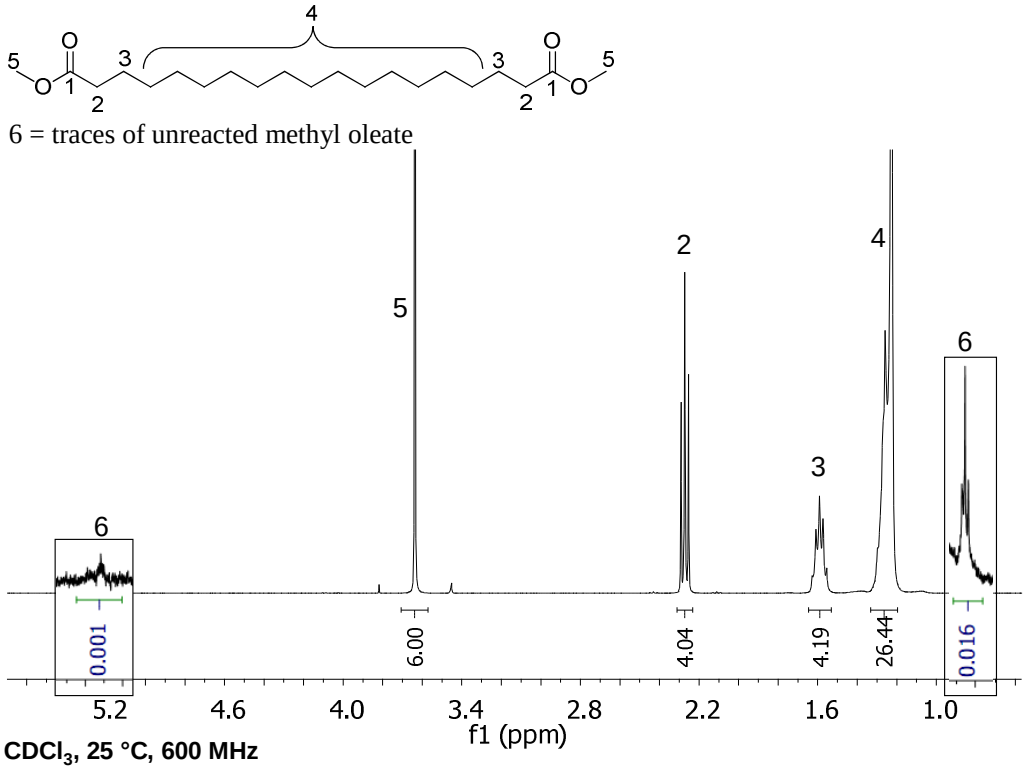


Figure 5.1 ^{1}H-NMR spectrum of isolated dimethyl-1,19-nonadecanedioate.

In further experiments the influence of reaction conditions on the reaction were studied (Table 5.1). The amount of catalyst applied seems to have some, albeit moderate influence on the yield obtained. When reducing the amount of catalyst from 1.6 to 0.2 mol-% the yield of the isolated product drops from 86 to 52 % (entries 6 and 8). This influence could be due to catalyst stability as during the reaction palladium(II) is reduced to catalytically inactive palladium(0) which precipitates from the reaction mixture in the form of aggregates of palladium black. The latter is unlikely to get reoxidised to palladium(II) by methanesulfonic acid. Alternatively, the carbonylation reaction may just be slow. The amount of dtbpx ligand applied has a greater influence. When reducing the amount of diphosphine ligand from a 3.5 to a 2.1-fold excess over $Pd(OAc)_2$, only traces of product were detected (entries 2 and 3). This is in agreement with previously reported findings on catalyst stability.[88, 100] A five-fold excess of the diphosphine ligand seems to be optimal for the isomerising alkoxycarbonylation of olefins. Therefore in all further experiments a diphosphine ligand to palladium ratio of five was chosen. When replacing the dtbpx ligand with the equally bulky and electron rich dtbpp ligand **2** (Scheme 3.3) the yield is considerably reduced from 21 % to 11 % at identical

reaction conditions (entries 9 and 10) thus identifying the dtbpx ligand as the so far most suitable ligand for the reaction.[38]

Table 5.1 Isomerising methoxycarbonylation of methyl oleate.

Entry	$Pd(OAc)_2$ / mmol	dtbpx / mmol	$MeSO_3H$ / mmol	methanol / mL	methyl oleate[a] / mmol	P / bar	T / °C	isolated yield[b,c]
1	0.13	0.48	0.96	10	6 (99 %)	20	40	76 % (76 %)
2	0.017	0.06	0.5	10	6 (99 %)	20	40	18 % (18 %)
3	0.017	0.036	0.5	10	6 (99 %)	20	40	> 2 %[d]
4	0.017	0.06	0.5	10	6 (99 %)	50	40	5 % (5 %)
5	0.017	0.06	0.5	10	6 (99 %)	50	90	44 % (44 %)
6	0.096	0.48	0.96	10	6 (99 %)	20	90	86 % (86 %)
7	0.096	0.48	0.96	10	6 (75 %)	20	90	38 % (51 %)
8	0.012	0.06	0.5	10	6 (99 %)	20	90	52 % (52 %)
9	0.012	0.06	0.5	10	6 (75 %)	20	90	21 % (28 %)
10	0.012	0.06[e]	0.5	10	6 (75 %)	20	90	11 % (15 %)

Methoxycarbonylations were performed in a 20 mL stainless steel autoclave 22 h. [a] purity of starting material given in brackets. [b] yield of pure (> 99 %) dimethyl-1,19-nonadecanedioate. [c] yield taking methyl oleate content into account given in brackets. [d] determined by GC. [e] dtbpp.

Higher reaction temperatures of 90 °C led to increased yields (entries 1 and 6). Other than in the alkoxycarbonylation polymerisation of 10-undecen-1-ol lower pressures of 20 bar are preferable over pressures of 50 bar. Higher pressure leads to higher carbon monoxide concentration which could hamper the reaction either due to catalyst decomposition by reduction of the palladium(II) or due to blocking of coordination sites by coordination. Surprisingly, even technical grade methyl oleate is suitable for the reaction and leads to satisfactory yields of 51 % with respect to the content of methyl oleate of 75 % in this starting material when applying a catalyst loading of 1.6 mol-% (entry 7). This yield represents the isolated yield, meaning of the > 99 % pure dimethyl-1,19-nonadecanedioate. The product still cleanly crystallises from the reaction mixture in spite of other saturated fatty acid esters present in the technical grade methyl oleate. From GC-MS measurements of the technical grade 75 % methyl oleate applied it was revealed that it contains the saturated fatty acid esters methyl myristate (C 14), methyl palmitate (C 16), methyl heptadecanoate and methyl stearate (C 18) as well as the unsaturated fatty acid esters methyl palmitoleate (C 16) and methyl heptadecenoate and furthermore the polyunsaturated fatty acid esters methyl linoleate and methyl linolenate. Köckritz and coworkers and later Cole-Hamilton and coworkers demonstrated the direct utilisation of high oleic sunflower oil in isomerising

methoxycarbonylation reactions. However higher catalyst concentrations of at least 2.4 mol-% were required.[101-102]

In conclusion, so far optimum conditions for the methoycarbonylation of methyl oleate were found to be a rather high catalyst loading of 1.6 mol-% palladium acetate with a five-fold excess of dtbpx ligand at 90 °C and 20 bar carbon monoxide pressure.

5.2 Isomerising Ethoxycarbonylation of Ethyl Erucate

The isomerising alkoxycarbonylation of erucates was performed analogous to that of methyl oleate. Preliminary experiments were performed in methanol starting from methyl erucate (Table 5.2, entry 3). Unfortunately, methyl erucate is insoluble in methanol due to its longer hydrocarbon chain and higher hydrophobicity thus forming a two phase reaction mixture, even at elevated temperatures. Nevertheless satisfactory yields of 68 % could be obtained. To further improve these yields the reaction was conducted in ethanol instead of methanol leading to a homogeneous reaction mixture (entries 4 and 5). Due to the presence of 0.3 mol-% methanesulfonic acid transesterification of the methyl ester occurred, mainly leading to the symmetrical diethyl-1,23-tricosanedioate instead of the unsymmetrical 1-ethyl-23-methyl-tricosanedioate. The transesterification was not complete which was revealed by ^{1}H-NMR spectroscopy (Figure 3.2) and it was not possible to separate the 1-ethyl-23-methyl-tricosanedioate from the diethyl-1,23-tricosanedioate, which is advantageous when applying this compound in condensation polymerisation. Undetermined amounts of the 1-ethyl-23-methyl-tricosanedioate do not lead to unreactive endgroups but hamper the adjustment of an exact stoichiometry and thus may hinder the formation of high molecular weight polymers.

Table 5.2 Isomerising ethoxycarbonylation of ethyl erucate.

Entry	$Pd(OAc)_2$ / mmol	dtbpx / mmol	$MeSO_3H$ / mmol	alcohol / mL	erucate[a] / mmol	P / bar	T / °C	isolated yield[b,c] / %
1	0.079	0.395	0.79	10[d]	4.93[e] (95 %)	20	90	75 % (79 %)
2	0.04	0.198	0.4	10[d]	4.93[e] (95 %)	20	90	51 % (56 %)
3[f]	0.079	0.395	0.79	10[g]	5.00[h] (90 %)	20	90	68 % (76 %)
4[i]	0.079	0.395	0.79	10[d]	4.93[h] (90 %)	20	90	79 % (88 %)
5	0.0099	0.049	0.099	10[d]	4.93[h] (90 %)	20	90	18 % (20 %)

Alkoxycarbonylations were performed in a 20 mL stainless steel autoclave for 22 h. [a] purity given in brackets. [b] yield of pure (> 99 %) diethyl-1,23-tricosanedioate. [c] yield taking purity of starting material into account given in brackets. [d] ethanol. [e] ethyl erucate. [f] product: tricosane-1,23-dimethylester. [g] methanol. [h] methyl erucate. [i] 114 h reaction time.

Therefore ethyl erucate was employed which also forms a homogeneous reaction mixture with ethanol. With a catalyst loading of 1.6 mol-% the reaction leads to good yields of 75 % of the more than 99 % pure diethyl-1,23-tricosanedioate (entry 1) which was confirmed by ^{1}H-NMR and ^{13}C-NMR spectroscopy and gas chromatography (Figure A 17, Figure A 18, Figure A 19). When reducing the catalyst loading to 0.08 mol-% reasonably good, isolated yields of 51 % were obtained (entry 2).

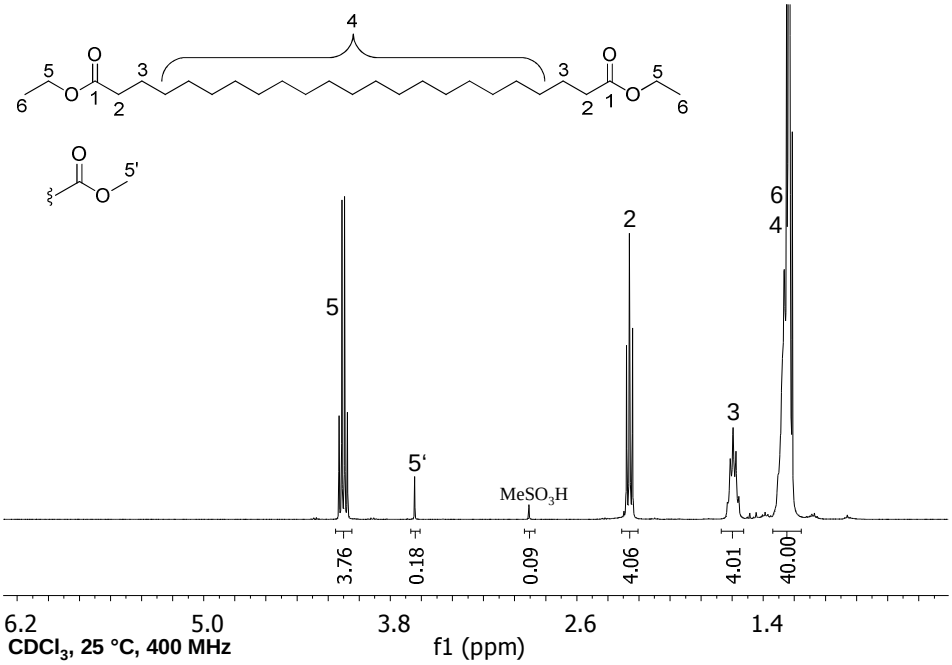


Figure 5.2 ^{1}H-NMR spectrum of diethyl-1,23-tricosanedioate from methyl erucate.

By comparison to the methoxycarbonylation of ethylene in the Alpha process,[29-30] the carbonylation of internal olefins is slower than the carbonylation of ethylene and thus more demanding on catalyst stability. The catalyst activity and lifetime are probably also dependent on the molar ratio of olefin and carbon monoxide. For the methoxycarbonylation of ethylene the molar ratio of ethylene to carbon monoxide dissolved in the liquid phase of the reaction should be preferably maintained at least at 5:1. Lower ratios lead to rapid deterioration in catalyst performance.[103] In the methoxycarbonylation of ethylene maintaining this ratio is relatively simple as the feed of the two gases can be adjusted and maintained along the reaction. In the alkoxycarbonylation of unsaturated fatty acid esters maintaining a constant molar ratio of olefin to carbon monoxide proves to be difficult as the olefin concentration in the reaction mixture continuously decreases along the reaction, whereas it is presumed that the carbon monoxide concentration remains approximately constant. More importantly, due to

the much higher molecular weight of fatty acid esters vs. ethylene their molar concentration is usually lower. Excess diphosphine ligand might protect the active catalyst from decomposition to some extent and might thus prolong the catalyst's lifetime. For maintaining the olefin concentration constant, a continuous feed of the liquid olefin into the pressurised autoclave would be necessary. Technically this is rather difficult to realise on a laboratory scale as it requires a continuous process or at least a semi batch process. However, this is a problem which can be solved on an industrial scale.

5.3 Preparation of Nonadecane-1,19-diol and Tricosane-1,23-diol

Beyond their direct utilisation as polycondensation monomers the α,ω-diesters are also of interest for the preparation of other difunctional compounds. The compounds most easily accessible thereof are the corresponding α,ω-diols. In preliminary studies reduction of the diesters to the corresponding diols was achieved by means of the inorganic hydride $LiAlH_4$. Due to the poor solubility of the long-chain diols in common organic solvents and their rather high melting and evaporation temperatures standard reduction procedures could not be applied. Usually the reduction of aliphatic esters is conducted in diethylether which is not possible for the preparation of nonadecane-1,19-diol and tricosane-1,23-diol as they are insoluble in diethylether, even at elevated temperatures. Therefore the reaction was carried out in THF which does not allow for aqueous workup for the removal of inorganic salts. Instead, the inorganic salts have to be precipitated and removed by filtration over a Büchner funnel at 40 °C as the diol products are soluble in THF only at elevated temperatures. Standard procedures for precipitation of lithium and aluminium salts involve dissolving in dilute acids followed by the addition of sodium hydroxide solution. This produces a voluminous precipitate which is filtered with difficulty and which also might trap some of the product.[104] A better way of precipitating the inorganic salts is the method described by Fieser et al.[105] Excess of reducing agent is quenched by slowly adding a calculated amount of water and 15 % sodium hydroxide. The application of *n* g of $LiAlH_4$ requires the successive addition of *n* mL of water, *n* mL of 15 % aqueous sodium hydroxide and *3n* mL of water. This produces a dry, granular precipitate which absorbs very little product and is easy to filter and wash and also does not dissolve in THF at elevated temperatures. In this way nonadecane-1,19-diol was obtained from dimethyl-1,19-nonadecanedioate in 93 % yield and tricosane-1,23-diol from diethyl-1,23-tricosanedioate in 87 % yield. Both compounds were isolated in a

purity suitable for step-growth polymerisations, which was confirmed by ^{1}H-NMR (Figure 5.3), ^{13}C-NMR spectroscopy and elemental analysis.

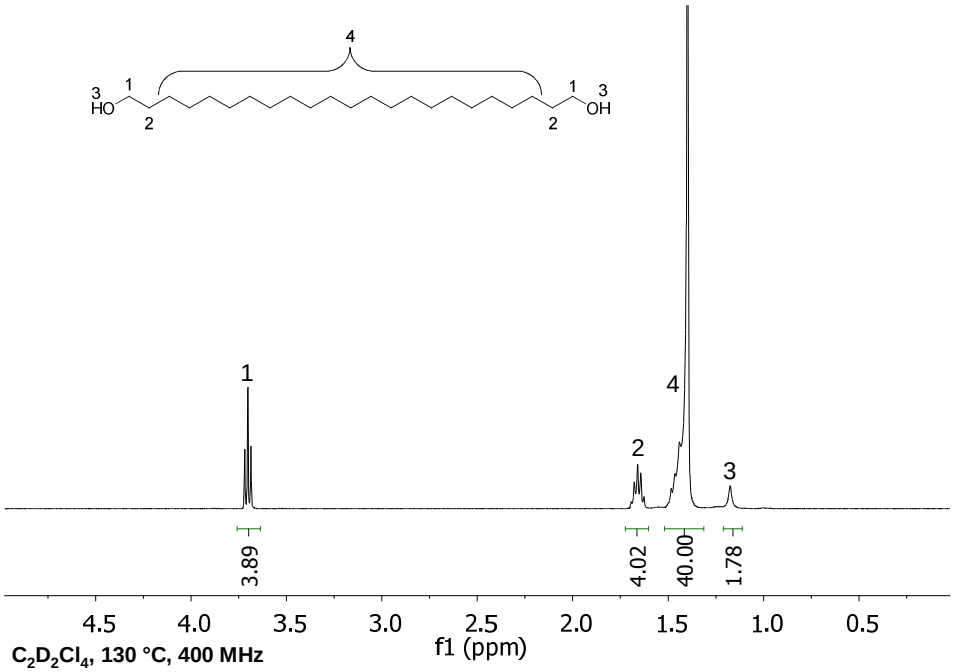
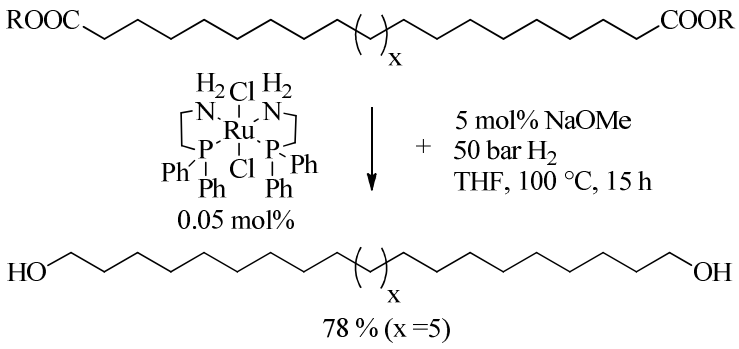


Figure 5.3 ^{1}H-NMR spectrum of tricosane-1,23-diol.

Yet, on a larger scale the cost of $LiAlH_4$, the poor atom economy and the work up procedure are serious drawbacks. An alternative route involving catalytic hydrogenation is desirable. The most well known, and until recently the only catalysts which allow the reduction of aliphatic esters to alcohols using hydrogen are a copper chromite catalyst, the so called Adkins catalyst,[106] and Raney nickel.[107] Unfortunately, both catalysts require rather high catalyst loadings of around 10 to 150 wt.-% and harsh reaction conditions of around 250 °C / 220 bar for copper chromite and 100 °C / 350 bar for Raney nickel. In 2007, Saudan et al. reported on a homogeneous dichlorobis[2-(diphenylphosphino)ethylamine]ruthenium catalyst[108-109] which reduces esters with hydrogen to alcohols under relatively mild conditions of 100 °C and 50 bar hydrogen pressure and low catalyst loading of 0.05 mol-% (Scheme 5.3).



Scheme 5.3 Catalytic hydrogenation of diethyl-1,23-tricosanedioate to tricoane-1,23-diol using dichlorobis[2-(diphenylphosphino)ethylamine]ruthenium.

The only minor disadvantage might be the supplementary addition of a base, in this case sodium methanolate, which is necessary as it presumably accelerates heterolytic hydrogen activation.[110] This catalyst system was found to be suitable for the reduction of long-chain aliphatic diesters like the diethyl-1,23-tricosanedioate. In contrast to the procedure described by Saudan et al. aqueous work up is not necessary as the tricosane-1,23-diol simply crystallises from the reaction mixture upon cooling to ambient temperatures. After filtration and recrystallisation the desired product was obtained in 78 % yield in purity suitable for step growth polymerisations.

5.4 Polyesterifications

For the synthesis of long-chain aliphatic polyesters from α,ω-functionalised C_{19} and C_{23} hydrocarbons obtained from oleic- and erucic acid esters, two routes are possible: either by transesterification polymerisation of the dicarboxylic acid esters obtained from the carbonylation of the unsaturated fatty acid esters or by direct polyesterification of the corresponding diacids. Although the hydroxyl-ester interchange reaction is much slower than the direct polyesterification this route was chosen for the synthesis of poly(1,19-nonadecadiyl-1,19-nonadecanedioate) and poly(1,23-tricosadiyl-1,23-tricosanedioate) as it does not require an additional chemical transformation, the hydrolysis of the dicarboxylic acid esters. The transesterification polymerisations were performed in bulk at elevated temperatures in the presence of a titanium alkoxylate catalyst thus affording poly(1,19-nonadecadiyl-1,19-nonadecanedioate) and poly(1,23-tricosadiyl-1,23-tricosanedioate) in molecular weights of typically M_n = 2 × 10^4 g mol^{-1} (M_w/M_n = 2), determined by GPC measurements in 1,2,4-trichlorobenzene at 160 °C versus linear polyethylene standards. This

value approaches typical molecular weights of commercial polyesters.[111] The general issues of polycondensation limits also apply to this reaction. For achieving high molecular weight polyesters the liberated alcohol has to get removed very efficiently. Already for small concentrations of the alcohol the reaction is in dynamic equilibrium prohibiting further increase of the molecular weight of the polyester. Efficient removal of liberated alcohol requires intensive mixing and a sufficient melt surface area. The higher the molecular weight of the desired polyester, the higher is its melt viscosity and the more difficult becomes the efficient removal of the liberated alcohol.

In the synthesis of polyesters from shorter chain dicarboxylic acids and diols, applying low pressures at the end of the polymerisation reaction can lead to the formation of macrocycles by backbiting as the cyclic product may be constantly removed.[112] However, excessive formation of macrocycles was not observed for the polyesters obtained from oleic- and erucic acid esters as the molecular weights determined by GPC match the molecular weights determined from ^{1}H-NMR spectra.

It is generally accepted, that in polyesterification reactions the metal ligands are exchanged with the carbonyl and hydroxyl groups present in the reaction medium.[60] Indeed, the formation of butyl ester end groups from $Ti(OBu)_4$ has been observed by ^{13}C-NMR spectra of poly(1,23-tricosadiyl-1,23-tricosanedioate) (cf. Figure 5.4). The unreactive endgroups from the catalyst precursor contribute to limited polymer molecular weights. However, they are not the single decisive factor as monomer based endgroups are also observed.

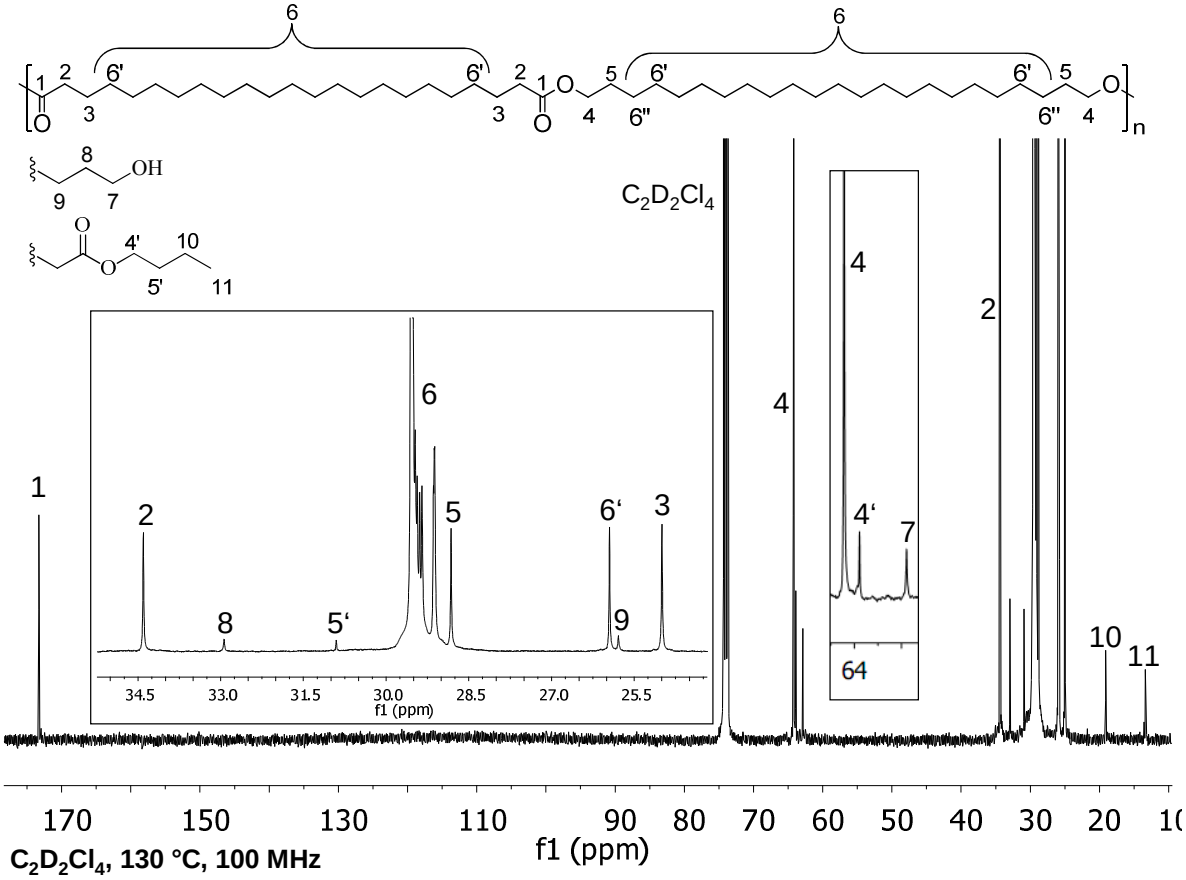


Figure 5.4 ^{13}C-NMR spectrum of poly(1,23-tricosadiyl-1,23-tricosanedioate) with butyl ester endgroups from the catalyst.

The characterisation of the polyesters obtained from oleic- and erucic acid esters by differential scanning calorimetry (DSC) revealed for the poly(1,19-nonadecadiyl-1,19-nonadecanedioate) a melt peak at T_m = 103 °C and a crystallisation peak at T_c = 87 °C with an enthalpy ΔH_m = 140 J g^{-1} (cf. Figure A 23). For poly(1,23-tricosadiyl-1,23-tricosanedioate) a melt peak at T_m = 99 °C and a crystallisation peak at T_c = 84 °C and a high[113] melt enthalpy ΔH_m = 180 J g^{-1} was found. These melting points compare for example with the ubiquitous thermoplastic low density polyethylene (LDPE). Wide angle X-ray scattering (WAXS) yields a high degree of crystallinity χ of about 70 % for poly(1,19-nonadecadiyl-1,19-nonadecanedioate) and about 75 % for poly(1,23-tricosadiyl-1,23-tricosanedioate) (cf. Figure A 24). From the ΔH_m determined by DSC and χ determined by WAXS an enthalpy of fusion ΔH_u of the crystalline portion of about 200 J g^{-1} for poly(1,19-nonadecadiyl-1,19-nonadecanedioate) and 240 J g^{-1} for poly(1,23-tricosadiyl-1,23-tricosanedioate) is estimated by comparison to ΔH_u = 293 J g^{-1} for linear polyethylene (cf. Figure 5.5 and Figure A 24). Poly(decamethylenesebacate) as an example of a long-chain linear aliphatic polyester from

traditionally accessible monomers melts with ΔH_u = 148 J g^{-1} (T_m = 80 °C).[113] These properties also approach those of linear polyethylene in terms of enthalpy per mass associated with melting, reflecting the predominantly hydrocarbon nature of the polymers.

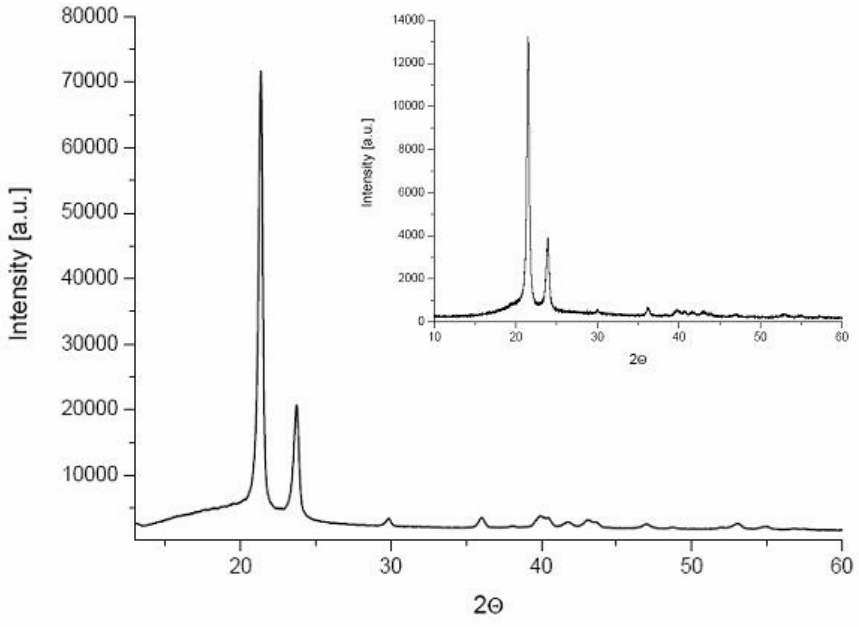
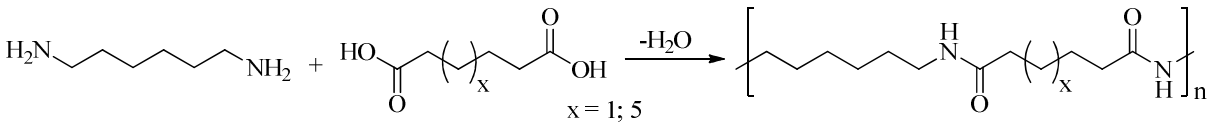


Figure 5.5 WAXS diffraction pattern of poly(1,23-tricosadiyl-1,23-tricosanedioate) and WAXS diffraction pattern of linear polyethylene for comparison (M_n = 8.7 ×10^4 g mol^{-1}; M_w/M_n = 2.2; T_m = 137 °C; χ ca. 75 %).

In conclusion, this approach to semicrystalline aliphatic polyesters allows for an efficient and complete incorporation of fatty acid esters. This complete molecular incorporation in a linear fashion is also beneficial for achieving substantial melting points of the resulting polyesters.

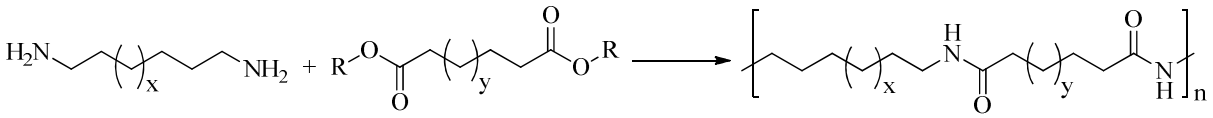
6 Aliphatic Polyamides from Methyl Oleate and Ethyl Erucate

In general, several routes for the preparation of plant oil based polyamides are possible. First, there is the standard procedure of reacting dicarboxylic acids with diamine components which is also an industrially proven process for the synthesis of for example Nylon-6,6 or Nylon-6,10 (Scheme 6.1).



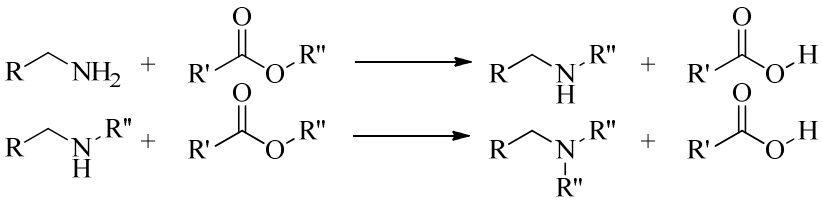
Scheme 6.1 Synthesis of polyamides from diamines and dicarboxylic acids.

Another possible route is the so called ester aminolysis,[114] where a dicarboxylic acid ester is reacted with a diamine under the formation of an amide and liberation of an alcohol, analogous to the transesterification route to polyesters (Scheme 6.2).



Scheme 6.2 Synthesis of polyamides from diamines and dicarboxylic acid esters (aminolysis).

In the present case this route is highly attractive as it would allow the direct utilisation of the α,ω-diesters obtained by the isomerising alkoxycarbonylation of the unsaturated fatty acid esters. Unfortunately, the few previously described examples of ester aminolysis polymerisation only yield short chained oligo-amides,[115-116] being due to the lower reactivity of carboxylic acid esters over their free acids, which autocatalyse the aminolysis reaction.[117] The lower activity mainly leads to low reaction rates in the later phase of the polycondensation reaction.[114] This could be overcome by conducting the reaction in the presence of a proton source, for example excess water[118] or catalytic amounts of phenol,[119] which probably leads to at least partial hydrolysis of the ester species.[120-121] However, the most important reason for the low molecular weight products when using alkyl esters is the competition of amidation and alkylation of the diamine by the diester leading to the formation of secondary and tertiary amines (Scheme 6.3) which no longer undergo a condensation reaction and thus represent unreactive chain ends. [122-123]



Scheme 6.3 Alkylation of amines by carboxylic esters.

Another problem of the aminolysis route is the adjustment of an exact stoichiometry. Considering all this, the dicarboxylic acids are preferable for polycondensation reactions, especially as the formation of the ammonium carboxylate salts, the so called nylon salts, from

the dicarboxylic acids and the diamines, allows the adjustment of an exact stoichiometry of these two reactants which is of utmost importance for achieving high molecular weights.

6.1 Preparation of Tricosane-1,23-dicarboxylic acid

Tricosane-1,23-dicarboxylic acid was synthesised by hydrolysis of diethyl-1,23-tricosanedioate with potassium hydroxide in methanol at elevated temperatures.[124] The reaction had to be conducted at 70 °C instead of 35 °C, as only at higher temperatures the diethyl-1,23-tricosanedioate is soluble in methanol. Also, longer reaction times of 10 hours instead of 60 minutes and a higher amount of KOH were required, adding up to a ratio of ester to KOH of 1 to 6 instead of 1 to 4. Recrystallisation from methanol provided the desired tricosane-1,23-dicarboxylic acid in 96 % yield and in more than 99 % purity as revealed by elemental analysis and ^{1}H-NMR spectroscopy (Figure 6.1).

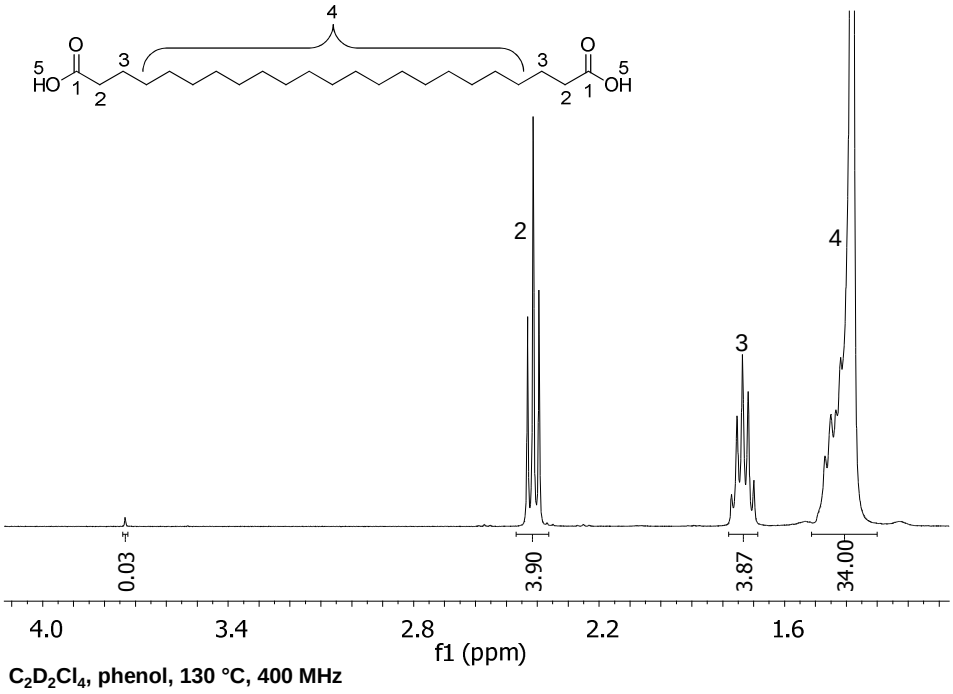


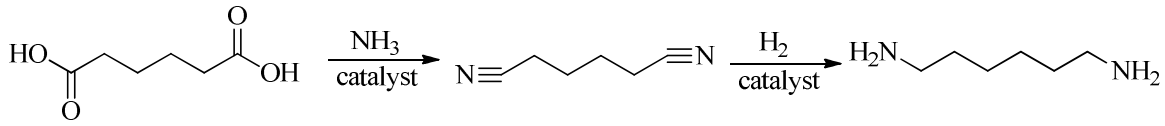
Figure 6.1 ^{1}H-NMR spectrum of tricosane-1,23-dicarboxylic acid.

Dissolving the long chain dicarboxylic acid for NMR experiments turned out to be difficult which is probably due to intermolecular hydrogen bonding in combination with the long apolar aliphatic chain. For other substances which can form intermolecular hydrogen bonds this problem is circumvented by utilising a hydrogen bond forming donor as solvent. Typical deuterated hydrogen bond donor solvents suitable and affordable for NMR spectroscopy are

methanol-d_4 and dmso-d_6. Unfortunately, both solvents are very polar solvents which are not compatible with the long apolar aliphatic chain of the tricosane-1,23-dicarboxylic acid. Therefore the sample was dissolved in tetrachloroethane-d_2 and excess non-deuterated phenol, serving as hydrogen bond donor, at 130 °C.

6.2 Preparation of Tricosane-1,23-diamine

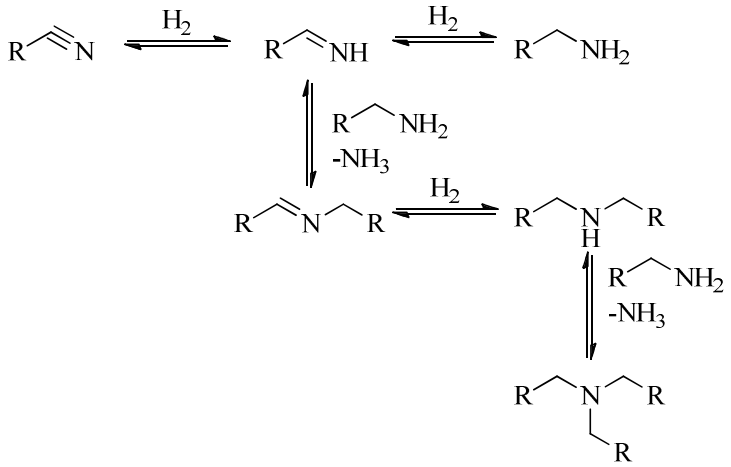
Higher primary aliphatic diamines are mainly applied in polyamide synthesis, the most common being hexamethylene-1,6-diamine. Although they are produced on an industrial scale, the selective synthesis of terminal primary amines is challenging due to their high reactivity. To date, there are several routes to primary aliphatic amines. The most common and also industrially proven ones start from the corresponding dinitriles.[125-126] Hexamethylene-1,6-diamine for example, a building block of Nylon-6,6, is produced from adipic acid which is reacted with ammonia at atmospheric pressure at 300-400 °C to form the corresponding adiponitrile (Scheme 6.4).



Scheme 6.4 Industrial synthesis of hexamethylene-1,6-diamine.

Unfortunately, the following catalytic hydrogenation of the adiponitrile to the desired hexamethylene-1,6-diamine is not entirely selective (Scheme 6.5). Side reactions resulting in the formation of secondary amines always occur, but can be suppressed by the addition of ammonia, sodium hydroxide solution, or acid.[125] Another possibility is the reduction by means of the inorganic hydride $LiAlH_4$, which is convenient only on a laboratory scale for reasons mentioned above. Thus, for the formation of long chain primary aliphatic amines the route via the dinitriles is very attractive. Drawbacks are the very high temperatures and the application of liquid ammonia in the nitrile formation, for which our lab is lacking appropriate apparatuses. An alternative is the application of aqueous ammonia in the presence of elemental iodine, which is also suitable for the formation of higher aliphatic dinitriles in very high yields of 99 %, but from the corresponding diols.[127-128] To test this reaction, it was first performed starting with the commercially available model compound dodecane-1,12-diol, analogous to the previously described procedure. In this way dodecane-1,12-dinitrile could be

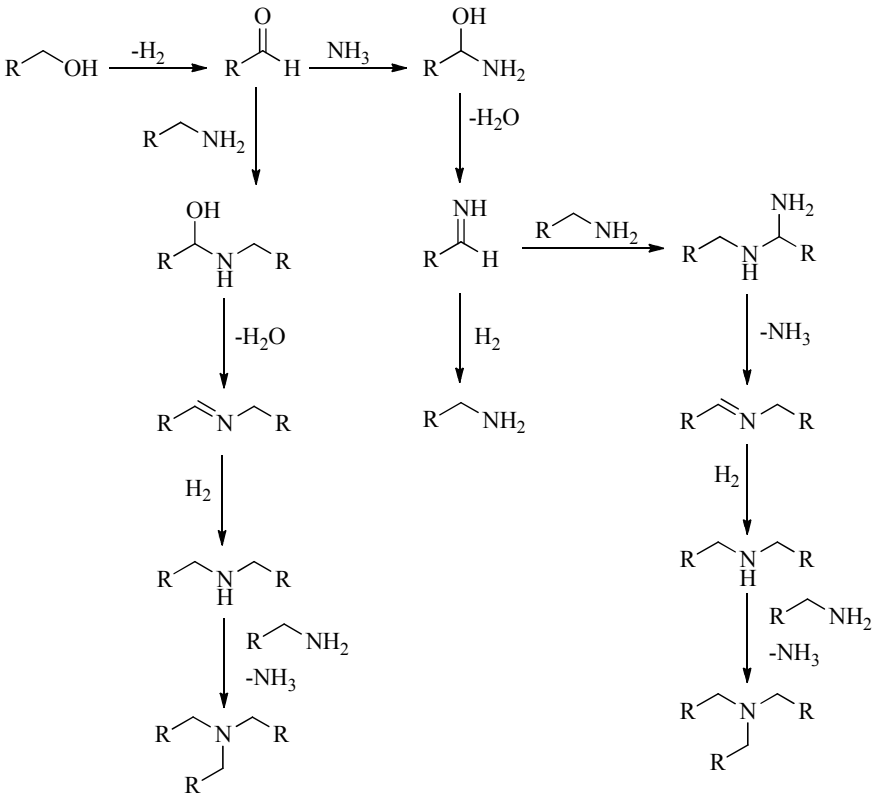
obtained in 79 % yield. The subsequent reduction applying $LiAlH_4$ only yielded 51 % of the dodecane-1,12-diamine. The reaction was conducted in diethyl ether in which the dodecane-1,12-diamine is only poorly soluble, even at elevated temperatures. This does not only complicate the work-up procedure involving the removal of the inorganic lithium and aluminium salts but probably also leads to partial precipitation of the α-amino-ω-nitrile species in the course of the reaction thus leading to limited yields. Reaction in THF, in which the dodecane-1,12-diamine is soluble at around 40 °C, should therefore lead to higher yields. It was assumed that this route is also suitable for the preparation of longer chain aliphatic diamines. Unfortunately, when applying nonadecane-1,19-diol instead of dodecane-1,12-diol under the same reaction conditions, only the starting material could be isolated. This is probably due to the higher hydrophobicity of the nonadecane-1,19-diol due to the longer hydrocarbon chain, which probably also leads to higher crystallinity and thus lacking solubility in aqueous ammonia. Therefore the reaction was repeated in a 20 mL stainless steel autoclave working at 90 °C. Under these conditions, conversion to the nitrile was observed but only about 40 % of the desired product were detected in the ^{1}H-NMR spectrum. This route to long chain aliphatic diamines based on plant oil fatty acids was therefore abandoned in favour of a more suitable one.



Scheme 6.5 Formation of primary, secondary and tertiary amines from nitriles.[125]

Primary amines are also accessible from the reaction of alcohols with ammonia. However, the product of this procedure is a mixture of primary, secondary and tertiary amines. Primary amines are more nucleophilic than ammonia and therefore compete with it during the reaction

with electrophiles present in the mixture, like aldehydes, which are formed by dehydrogenation of the alcohol as the initial and also rate determining step (Scheme 6.6).

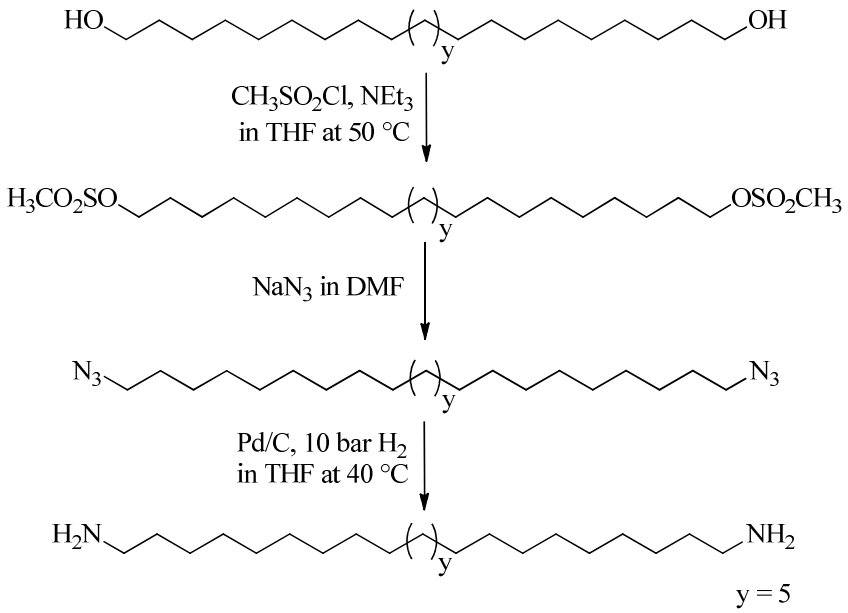


Scheme 6.6 Formation of primary, secondary and tertiary amines from alcohols.[125]

Furthermore the primary amine formation is thermoneutral whereas the secondary and tertiary amine formations are exothermic and thus thermodynamically favoured. The formation of secondary and tertiary amine can be suppressed to some extent by working with excess ammonia and by adjusting the reaction temperature. In general, rather harsh conditions of 5 to 250 bar pressure and temperatures of 100-250 °C are applied.[125] Recently Milstein and coworker presented a novel ruthenium pincer complex capable of efficiently catalysing the very desirable and atom efficient reaction of liquid ammonia with alcohols to selectively form primary amines and water under relatively mild reaction conditions of 7.5 bar and 135 °C. For primary aliphatic amines a selectivity of around 80 % was reported.[129] Unfortunately the reaction is described in a solvent mixture of water and dioxane which is unsuitable for tricosane-1,23-diol. Moreover distillation of the product would be necessary as the major side product is the corresponding acid. In difunctional compounds this means the occurrence of three different products, the desired diamine, a diacid and an α-amino-ω-acid. Distillation of

the tricosane-1,23-diamine probably would lead to considerable decomposition and therefore limited yields as for tricosane-1,23-diamine very high boiling points are expected. Also polycondensation should occur. Column chromatography is not to recommend as aliphatic diamines are not very well soluble in common organic solvents. Therefore this route was also dismissed as being unsuitable for the synthesis of tricosane-1,23-diamine. Köckritz and coworkers presented the formation of nonadecane-1,19-diamine from the corresponding diol and ammonia using the Milstein ruthenium pincer catalyst system working in 2-methyl-2-butanediol as solvent. Interestingly they could obtain the desired product in 68 % yield after Kugelrohr distillation, however without commenting on its final purity.[101, 130] Beller and coworkers reported on a similar method for obtaining primary amines. They employed $[Ru(CO)ClH(PPh_3)_3]$ as a catalyst precursor in the presence of xantphos working at 130-170 °C in tert-amylalcohol as solvent. However, this reaction is particularly suitable for secondary alcohols.[131]

A further possible route is the reduction of the corresponding amides. This route suffers from harsh reaction conditions and more important, lacks selectivity and thus results in a mixture of products. On a laboratory scale and for the synthesis of the very long chain aliphatic diamine from erucic acid the aforementioned routes are not recommendable due to the partially rather harsh reaction conditions and the mostly inevitable purification problems arising from the insufficient selectivity of the reactions towards the primary amines. Therefore a multi step route involving classical organic chemistry high conversion transformations was chosen for obtaining the desired tricosane-1,23-diamine in high yields in a purity suitable for condensation reactions (Scheme 6.7).



Scheme 6.7 Transformation of α,ω-diols into α,ω-diamines.

The synthesis was conducted analogous to a literature procedure for the synthesis of icosane-1-amine and docosane-1-amine[132] starting from the corresponding alcohol. First, tricosane-1,23-diol was transformed into the corresponding dimesylate by modifying the previously described reaction conditions by working in THF instead of dichloromethane and at 50 °C instead of 35 °C, as only under these conditions tricosane-1,23-diol is completely soluble, thus providing a homogeneous reaction mixture. The tricosane-1,23-dimesylate was then substituted to the azide which could be catalytically reduced to the desired tricosane-1,23-diamine. The catalytic reduction however also had again to be conducted under adjusted reaction conditions of 40 °C over room temperature, 10 bar hydrogen over 4 bar, and in THF instead of hexane. The crude product simply could be purified by recrystallisation from ethanol. In this way tricosane-1,23-diamine could not only be obtained in 64 % overall yield, but also in a purity suitable for condensation reactions, which was confirmed by ^{1}H-NMR spectroscopy (Figure 6.2).

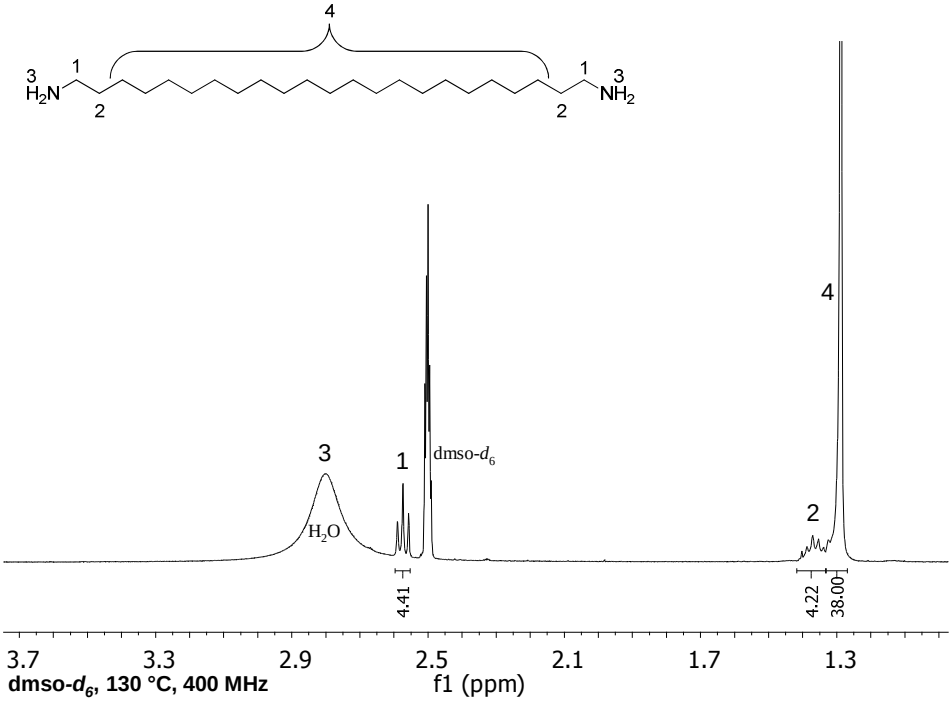
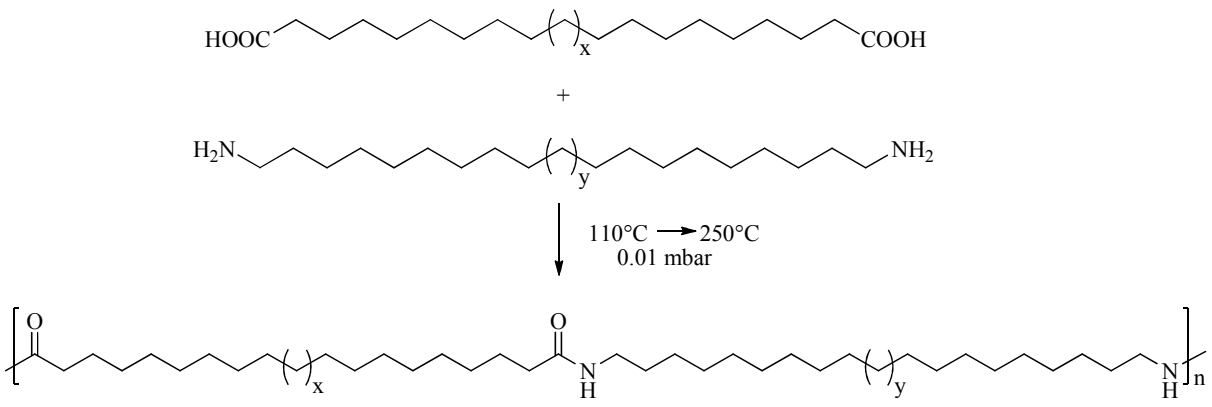


Figure 6.2 ^{1}H-NMR spectrum of tricosane-1,23-diamine.

6.3 Polycondensations

Plant oil based aliphatic polyamides were synthesised by polycondensation of α,ω-dicarboxylic acids and α,ω-diamines (Scheme 6.8). From nonadecane-1,19-dicarboxylic acid, tricosane-1,23-dicarboxylic acid, tricosane-1,23- diamine and the commercially available undecane-1,11-diamine and dodecane-1,12-diamine the polyamides PA 11 19, PA 11 23, PA 12 19, PA 12 23, PA 23 19 and PA 23 23 were obtained (Table 6.1).



Scheme 6.8 Polycondensation of plant oil based α,ω-diacids and α,ω-diamines to long-chain aliphatic polyamides.

^{1}H-NMR spectra (cf. Figure 6.5) revealed in all examples lower amounts of amine end-groups compared to carboxylic acid end-groups. In the course of the condensation reaction deposition of an off-white solid in the upper third of the schlenk tube in which the condensation reaction was conducted was observed. It is known from aliphatic amines that they are more volatile than their corresponding acids especially at the high temperatures employed at reduced pressure. For the synthesis of PA 11 23, PA 12 23 and PA 23 23 a small excess of the diamine species was therefore added. Conducting the condensation under reduced pressure in the later stages of the reaction leads to efficient removal of the water formed and thus to higher molecular weights.

For PA 6 6 it has been reported that synthesis at high temperatures under high vacuum and anhydrous conditions can result in coloured and crosslinked polymers, as under these conditions degradation reactions may occur.[70, 133-135] Brown colouring of some of the polyamides listed in Table 6.1 hints at the occurrence of side reactions during their synthesis. However, no side products could be identified from NMR spectroscopy as due to the addition of non deuterated phenol, to enable dissolving of the samples, the quality of the spectra is rather poor. The concentration of functional groups which might originate from side reactions is too low in these solutions to afford any signals in ^{13}C-NMR or two dimensional NMR spectroscopy. PA 12 23 which was kept under vacuum at its maximum reaction temperature for the shortest amount of time (cf. Table 9.1 in the experimental section) exhibits the lightest colour and also the highest molecular weight suggesting low amounts of or no side reactions.

Table 6.1 Plant oil based aliphatic polyamides.

Entry	polyamide	Integral[a] 3.0 ppm (^{1}H-NMR)	Integral[b] 2.4 ppm (^{1}H-NMR)	M (repeat unit)/ g mol^{-1}	$M_n \times 10^4$ (NMR)/ g mol^{-1}	T_m / °C	CH_2/CONH	colour
1	PA 11 19	3.6	9.3	478	0.4	167	14	brown
2	PA 11 23	0.5	10.6	534	0.5	167	16	beige
3	PA 12 19	-	5.1	492	1.0	169	14.5	light brown
4	PA 12 23	-	5.1	548	1.1	168	16.5	beige
5	PA 23 19	-	7.4	646	0.9	156	20	brown
6	PA 23 23	1.0	4.4	702	1.3	151	22	light brown

[a] CH_2 next to primary amine end group. The value of the integral of the signal at 3.3 ppm was set to 100.
[b] CH_2 next to carboxyl end group. The value of the integral of the signal at 3.3 ppm was set to 100.

As expected, the obtained polyamides show melting temperatures which are significantly lower than the melting temperatures of PA 6 6 or PA 6 10 which are at 265 °C and 222 °C.[69] This is due to their significantly higher amount of methylene groups and thus lower amide

group content compared to PA 6 6 and PA 6 10 which have a methylene to amide group ratio of 5 and 7. Also the effect of amide group distribution on the melting temperature is still valid at very high methylene contents. The odd-odd polyamide PA 11 19 (entry 1 Table 6.1) exhibits with 167 °C a considerably lower melting temperature than PA 6 24 with 189 °C.[136] Both polyamides have a ratio of methylene to amide groups of 14. In PA 11 19 the distribution of methylene groups between acid and amine component is almost equal whereas in PA 6 24 the diamine is considerably shorter than the dicarboxylic acid. With increasing methylene group content the melting temperatures indeed approach the melting temperatures of polyethylene but the hydrogen bonds still predominate polymer properties. In DSC measurements of aliphatic polyamides the melting transition is often not a single transition. Upon heating, solid state transitions[66] can take place in the unit cell, the lamellae can thicken, and secondary crystallisation can also take place.[70] Some of the DSC traces of the synthesised polyamides exhibit an exothermal transition after the melting transition during first heating (cf. Figure 6.3). Normally, this kind of transition is attributed to decomposition of the sample. In this case also proceeding of the polymerisation is possible.

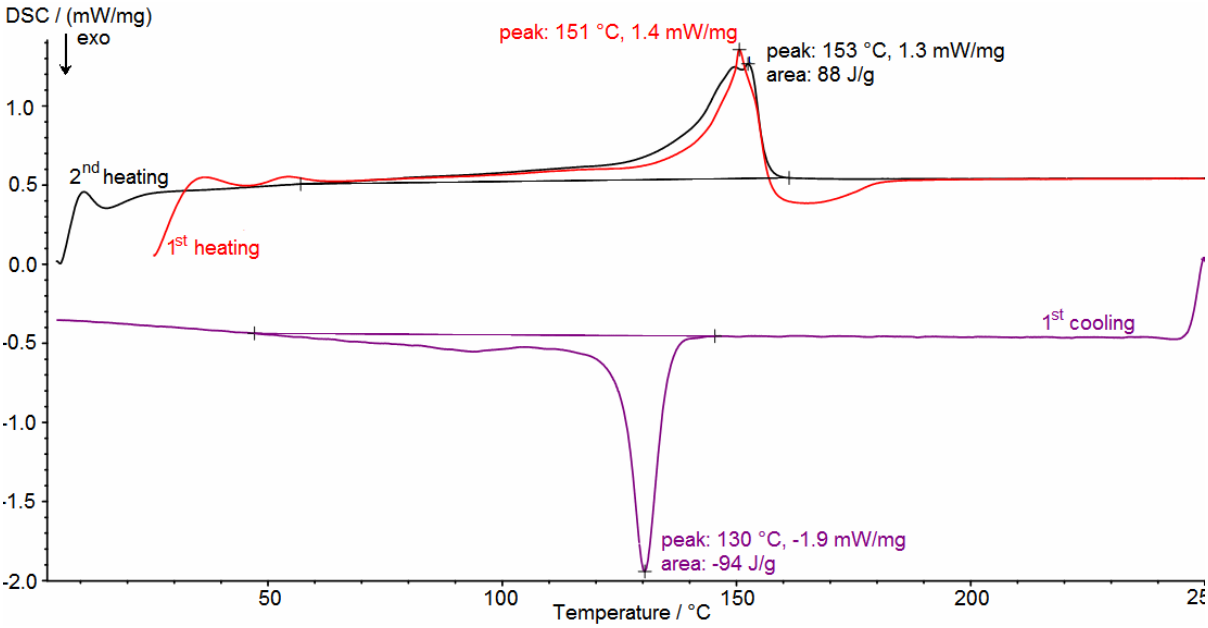


Figure 6.3 DSC trace of PA 23 23.

WAXS diffraction patterns were recorded on samples solidified by cooling from the melt. In such polyamide samples usually only very small, mostly defective crystals occur which is why WAXS diffraction patterns are usually recorded on drawn fibers or solution crystallised

samples. It is also well known from literature that in polyamides up to three crystal phases can coexist at room temperature.[69, 137] All polyamides in this work exhibited several, to some extent even sharp reflections, also hinting at the presence of more than one crystal modification (cf. Figure 6.4).

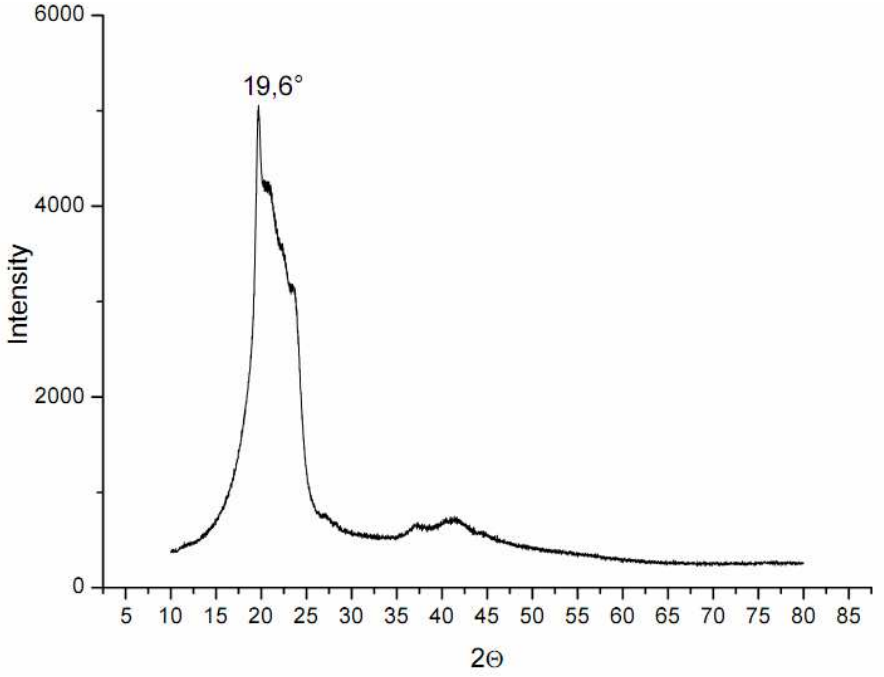


Figure 6.4 WAXS diffraction pattern of PA 23 23.

The obtained polyamides were insoluble in common organic solvents and also in solvents commonly known for polyamides like 1,1,1,3,3,3-hexafluoroisopropanol, sulphuric acid or *m*-cresol. This is due to their rather large content of linear aliphatic chains which are very apolar. However, for breaking up the inter-chain hydrogen bonds a hydrogen bond donor solvent, like the solvents named above which are commonly also very polar, is required. All polyamides obtained are soluble in 1,1,2,2-tetrachloroethane at 130 °C under addition of small amounts of phenol acting as hydrogen bond donor.

Therefore polymer molecular weights were determined from ^{1}H-NMR spectra recorded in 1,1,2,2-tetrachloroethane-d_2 at 130 °C (Figure 6.5).

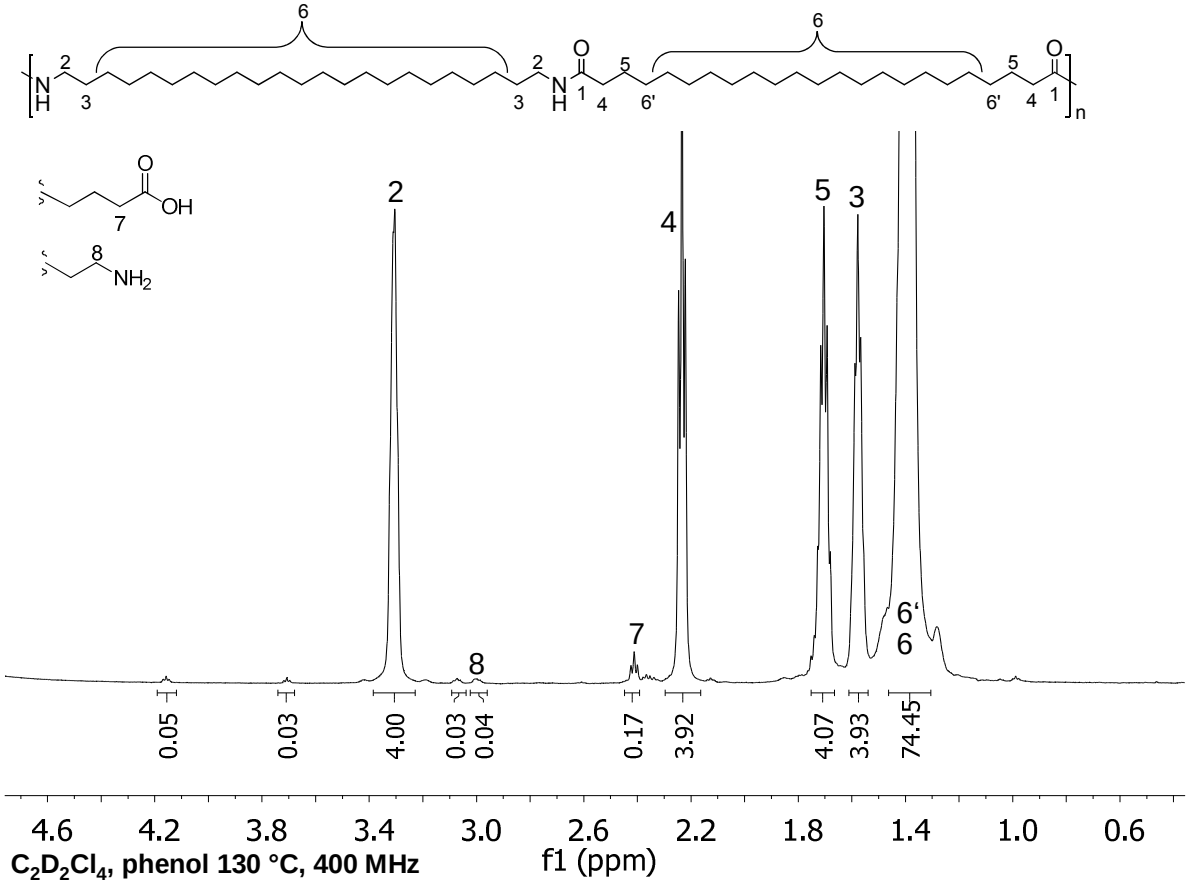


Figure 6.5 ^{1}H-NMR spectrum of PA 23 23.

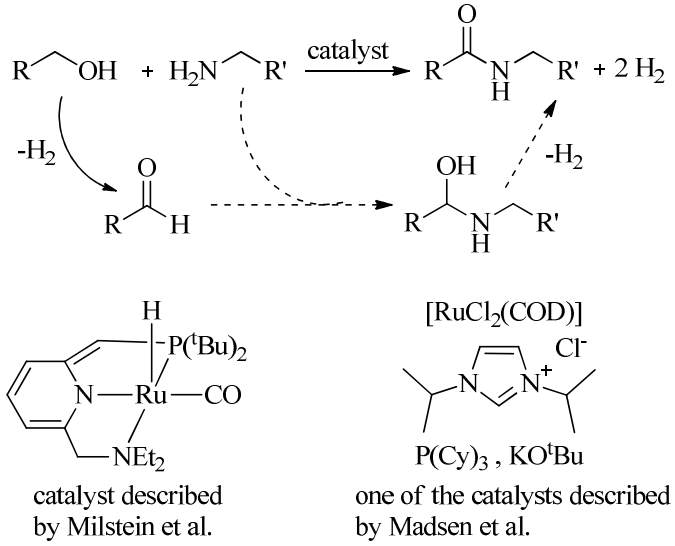
For calculations of polymer molecular weights from their ^{1}H-NMR spectra the ratio of the integral of a signal characteristic of the polymer backbone and the sum of integrals of signals characteristic of the end groups has to be formed. This ratio gives the average number of repeat units present in the polymer which is then multiplied with the molecular weight of the repeat unit to give the number average molecular weight of the polymer. In the present case the signal at around 3.3 ppm (2 in Figure 6.5) represents the polymer backbone and the signals at 3.0 ppm and 2.4 ppm (8 and 7 in Figure 6.5) represent the amine and carboxylic acid end groups of the polyamide.

$$M_n = \frac{\int signal\ at\ 3.3\ ppm}{\int signal\ at\ 3.0\ ppm + \int signal\ at\ 2.4\ ppm} \times M\,(repeat\ unit)$$

For the synthesised polyamides molecular weights from M_n = 0.4 × 10^4 g mol^{-1} to 1.3 × 10^4 g mol^{-1} were estimated.

Another possible route to amides is the ruthenium catalysed reaction of alcohols with amines under liberation of hydrogen which was reported by Milstein and coworkers in 2007[138] and later by Madsen[139-140] and Hong[141] (Scheme 6.9). The described ruthenium catalysts all afford very high yields in the formation of aliphatic amides. This makes them very interessting for the synthesis of aliphatic polyamides.

Recently, Guan and coworkers reported on the direct synthesis of polyamides by ruthenium catalysed dehydrogenation of diols and diamines utilising the ruthenium complex described by Milstein et al.[142] They synthesised a number of polyamides with polymer molecular weights of up to 2.8×10^4 g mol^{-1} in anisole or anisole DMSO solutions. All the polyamides they synthesised were soluble in these solvents or solvent mixtures.



Scheme 6.9 Formation of amides from alcohols and amines.

In this work dodecane-1,12-diol and dodecane-1,12-diamine were reacted without addition of a solvent in the melt in the presence of a catalyst consisting of [$RuCl_2$(cod)], KO^{t}Bu, 1,3-diisopropylimidazoliumchloride and tricyclohexylphosphine (cf. Scheme 6.9). The obtained polyamide was examined by DSC exhibiting a melt peak T_m = 179 °C at first heating and T_m = 172 °C at second heating, which is slightly lower than previously reported.[143] This could be due to the rather low molecular weight of only around 1.2×10^3 g mol^{-1} which was determined from ^{1}H-NMR spectroscopy. This also reveals that only very small amounts of alcohol remain unreacted and the major endgroup is the amine. Even small amounts of aldehyde were detected as well as ester and most likely carboxylic acid (Figure 6.6). The

reaction, however, was not studied in greater detatil and the reaction conditions were not optimised.

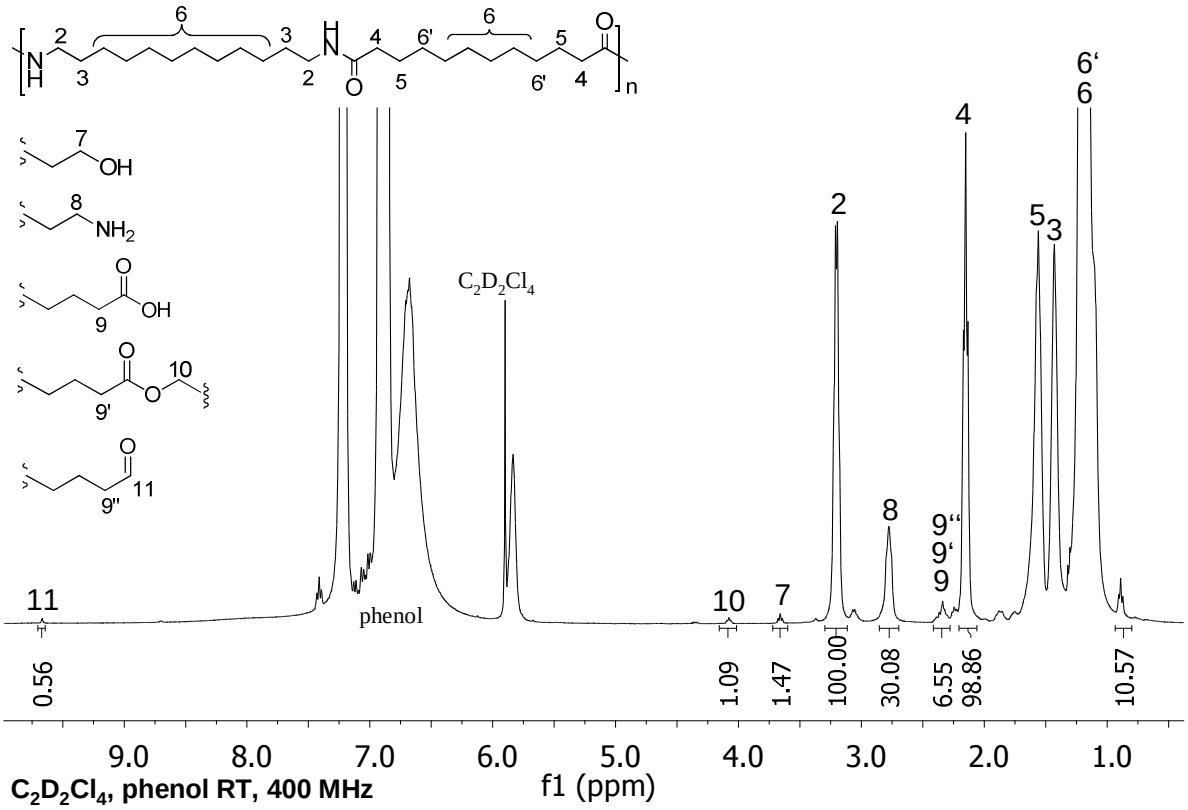


Figure 6.6 ^{1}H-NMR spectrum of PA 12 12.

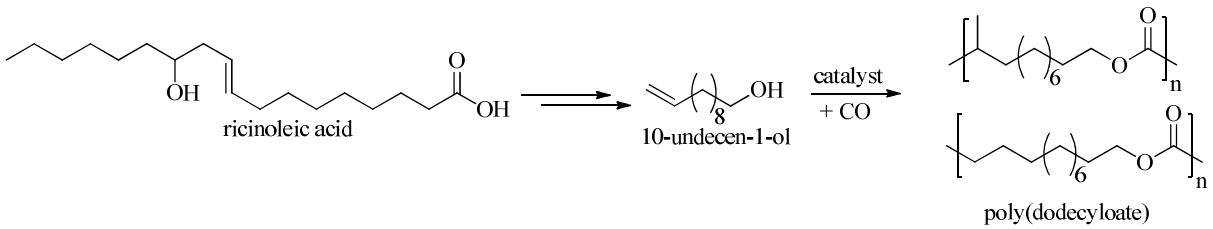
In general, it was demonstrated that novel long chain aliphatic polyamides are accessible from plant oils by complete incorporation of the starting fatty acid esters into the polymer molecule. The thus obtained polyamides exhibit substantially lower melting points than the ubiquitous PA 6 and PA 6 6 approaching that of polyethylene.

7 Summary and Conclusion

Today's polymer production relies almost exclusively on fossil feedstocks. This applies particularly to thermoplastic polymers, which represent the largest type of industrial polymers before thermosets and elastomers. In view of the limited range of fossil feedstocks, polymers prepared from alternative renewable resources are desirable on the long term. Fatty acids from plant oils are attractive substrates for polymers as they contain long chain linear segments.

As attractive as plant oils might occur as renewable feedstock they are indeed not low-cost raw materials and their prices are, often due to political decisions, subject to rather strong fluctuations. Although prices for ethylene and naphta have been continuously increasing over the last years, 'almost-as-good-as' replacements of existing fossil feedstock based products with products made from renewable resources will be difficult to achieve. Therefore the performance profile of plant oil based materials should be geared towards specific applications which are ideally unique to this feedstock.

Unsaturated plant oils provide, after transesterification or hydrolysis under liberation of glycerol, long-chained molecules with at least two functional groups which are accessible to chemical reactions. Ricinoleic acid, a common fatty acid and the major component of castor oil, can undergo thermally induced rearrangement affording 10-undecen-1-ol. Alkoxycarbonylation of an ω-unsaturated alcohol is a known route to the cyclic lactone by ring closure, but it can in principle also resemble an AB step growth polymerization. Therefore the preparation of poly(dodecyloate) from the castor oil derived 10-undecen-1-ol by alkoxycarbonylation polymerisation was investigated (Scheme 7.1). In a first approach the alkoxycarbonylation polymerisation of 10-undecen-1-ol was conducted utilising a cobalt carbonyl complex with a pyridine promoter as catalyst. In this entirely chemical route not involving any fermentation, plant oil based poly(dodecyloate) with about 20 to 30 % methyl branched repeat units, polymer molecular weights of $M_w = 5 \times 10^4$ g mol^{-1} and melting temperatures around T_m = 65 °C was obtained.



Scheme 7.1 Formation of poly(dodecyloate) from ricinoleic acid.

Control over the polymer microstructure und thus thermal properties was achieved by utilising a palladium complex with different mono- and bidentate phosphine ligands and methanesulfonic acid as catalyst. The lowest degrees of branching of around 3 % and thus the highest melting temperatures of T_m = 76 °C and T_m = 71 °C were obtained with the 1,3-bis(di-*tert*-butylphosphino)propane (dtbpp) and 1,3-bis(trioxa-adamantylphosphino)propane ligands. The highest degree of branching of around 32 % was obtained with the triphenylphosphine (PPh_3) ligand. The resulting polyester exhibited rather complex melting behaviour with two maxima at T_m = 58 °C and T_m = 66 °C. It also appears as if in this approach low amounts of branches and thus higher melting temperatures can only be achieved at the expense of reduced polymer molecular weights.

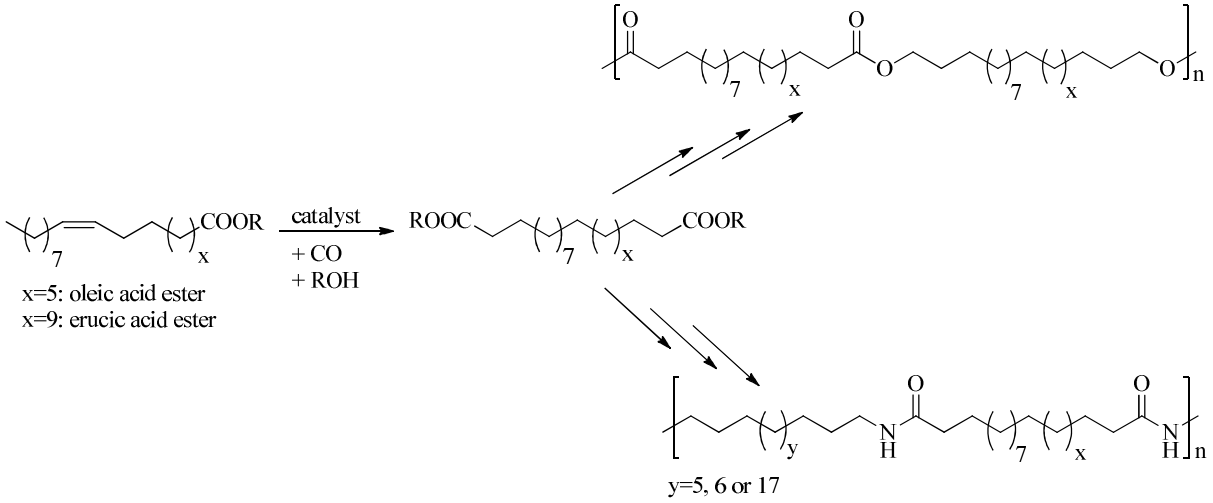
For complete utilisation of fatty acid esters in the generation of renewable resource based polymers a functionalisation at the chain end is required. However, in unsaturated fatty acid esters the double bond is an internal one. In the presence of catalytic amounts of $Pd(OAc)_2$, 1,2-bis[(di-*tert*-butylphosphino)methyl]benzene and methanesulfonic acid the selective alkoxycarbonylation of internal olefins under the exclusive formation of the terminal ester product is possible. Isomerising alkoxycarbonylation of methyl oleate and ethyl erucate, yielded dimethyl-1,19-nonadecanedioate and diethyl-1,23-tricosanedioate in > 99 % purity, respectively.

The thus obtained linear long chain carboxylic acid esters were transformed into the corresponding diols either by reduction with $LiAlH_4$ or by dichlorobis[2-(diphenylphosphino)ethylamine]ruthenium catalysed hydrogenation. In both cases the desired long chain diols were obtained in > 99 % purity.

Polycondensation of dimethyl-1,19-nonadecanedioate with nonadecane-1,19-diol afforded the novel poly(1,19-nonadecadiyl-1,19-nonadecanedioate) with molecular weights M_w of typically 2×10^4 g mol^{-1}, a melt peak temperature of T_m = 103 °C, a crystallisation temperature of T_c = 87 °C with an enthalpy of ΔH_m = 140 J g^{-1} and a degree of crystallinity of about 70 %. Poly(1,23-tricosadiyl-1,23-triosanedioate) from the linear terminal C_{23} diacid ester and diol respectively was obtained with $M_w = 2 \times 10^4$ g mol^{-1}, T_m = 99 °C, T_c = 84 °C and a high melt enthalpy ofΔH_m = 180 J g^{-1} and a crystallinity of around 75 %.

Diethyl-1,23-tricosanedioate obtained by alkoxycarbonylation of ethylerucate was also transformed into the corresponding dicarboxylic acid by hydrolysis and into the corresponding diamine in a four-step route. From the C_{23} and the commercially available C_{19} dicarboxylic acid and the C_{23} diamine as well as the commercially available C_{11} and C_{12} diamines the novel polyamides PA 11 19, PA 11 23, PA 12 19, PA 12 23, PA 23 19 and

PA 23 23 were generated (Scheme 7.2). The polyamides were obtained with molecular weights of around $M_n = 10^4$ g mol^{-1}. Polyamides PA 23 19 and PA 23 23, based on tricosane-1,23-diamine, exhibit a T_m = 156 °C and T_m = 152 °C, respectively. For polyamides PA 11 19, PA 11 23, PA 12 19 and PA 12 23 from the shorter chain diamino-1,11-undecane or diamino-1,12-dodecane with nonadecane-1,19-dicarboxylic acid and tricosane-1,23-dicarboxylic acid, as expected higher melting points between T_m = 167 °C and T_m = 169 °C were found.



Scheme 7.2 Formation of polyesters and polyamides from oleic and erucic acid esters.

The approach presented allows an efficient and complete incorporation of the plant oil fatty acid's long hydrocarbon chains into semicrystalline polyesters and polyamides. This complete molecular incorporation in a linear fashion is beneficial for achieving substantial melting points in aliphatic polyesters. In aliphatic polyamides the long hydrocarbon chains lead to considerably lower melting temperatures as known for to date industrially established aliphatic polyamides. In general, with increasing hydrocarbon content in polycondensates their melting temperatures approach the value of polyethylene, as the effect of functional groups, namely the disturbance of crystallisation by ester groups or the increased inter-chain interactions via hydrogen-bonding between amide groups, decreases.

The generic reaction types employed for the synthesis of novel, renewable resource based polycondensates in this work, namely carbonylation,[29] reduction and polycondensation[63, 111] are proven on large industrial scales.

8 Zusammenfassung

Heutzutage stützt sich die Herstellung von Polymeren fast ausschließlich auf fossile Ausgangsmaterialien. Das betrifft vor allem thermoplastische Polymere, welche vor Duroplasten und Elastomeren den größten Anteil an großtechnisch hergestellten Polymeren ausmachen. Im Hinblick auf die begrenzte Reichweite von fossilen Rohstoffen ist die Herstellung von Polymeren auf Basis nachwachsender Rohstoffe auf lange Sicht äußerst wünschenswert. Fettsäuren aus Pflanzenölen stellen attraktive Ausgangsverbindungen für Polymere dar, weil sie langkettige lineare Abschnitte enthalten. So vielversprechend wie Pflanzenöle als nachwachsende Rohstoffe auch erscheinen mögen, sind es jedoch keine extrem kostengünstigen Rostoffe. Ihre Preise sind oft, auch durch politische Entscheidungen, starken Schwankungen unterworfen. Obwohl die Preise für Ethylen und Naphta über die letzten Jahre hinweg stetig angestiegen sind, wird der Ersatz von bestehenden, aus fossilen Rohstoffen hergestellten Materialien mit auf nachwachsenden Rohstoffen basierenden Materialien, die aber nur beinahe so gut sind wie die erdölbasierten, schwierig sein. Daher sollte das Eigenschafts- und Einsatzprofil von pflanzenölbasierten Materialien in Richtung von Spezialanwendungen ausgelegt sein, die idealerweise auch einzigartig für diese Art von Rohstoff sind.

Ungesättigte Pflanzenöle liefern, nach Umesterung oder Hydrolyse unter Freisetzung von Glyzerin, langkettige Kohlenwasserstoffe mit mindestens zwei funktionellen Gruppen, die für chemische Reaktionen zugänglich sind. Rizinusöl, eine gängige Fettsäure und der Hauptbestandteil von Rizinusöl, kann eine thermisch induzierte Umlagerungsreaktion eingehen, welche 10-undecen-1-ol liefert. Die Alkoxycarbonylierungsreaktion eines ω-ungesättigten Alkohols ist eine bekannte Syntheseroute zu zyklischen Lactonen durch Ringschluss. Sie kann jedoch auch grundsätzlich einer Stufenwachstumsreaktion vom AB-Typ ähneln. Daher wurde die Herstellung von Poly(dodecyloat) aus 10-undecen-1-ol, welches aus Rizinusöl gewonnen wurde, durch die Alkoxycarbonylierungspolymerisation näher untersucht (Abbildung 8.1). In einem ersten Ansatz wurde die Alkoxycarbonylierungs-polymerisation mit Hilfe eines Cobaltcarbonylkomplexes als Katalysator mit Pyridin als Promotor durchgeführt. Auf diesem rein chemisch synthetischen Wege, der ohne Gärprozesse auskommt, konnte Poly(dodecyloat) aus Pflanzenöl mit circa 20 bis 30 % Methylverzweigungen in den Wiederholeinheiten, einem Molekulargewicht $M_w = 5 \times 10^4$ g mol^{-1} und einem Schmelzpunkt von $T_m = 65$ °C erhalten werden.

Die Polymermikrostuktur und damit die thermischen Eigenschaften des Polymers konnte durch die Verwendung eines Palladiumkomplexes mit unterschiedlichen ein- und zweizähnigen Phosphanliganden und Methansulfonsäure als Katalysator gezielt eingestellt werden. Der niedrigste Verzweigungsgrad von circa 3 % und somit die höchsten Schmelztemperaturen von T_m = 76 °C und T_m = 71°C wurden mit dem 1,3-bis(di-*tert*-butylphosphino)propan (dtbpp) und dem 1,3-bis(trioxa-adamantylphosphino)propanliganden erhalten. Der höchste Verzweigungsgrad von circa 32 % wurde mit dem Triphenylphosphanliganden (PPh_3) erhalten. Die so erhaltenen Polyester zeigten ein komplexes Schmelzverhalten mit zwei Maxima bei T_m = 58 °C und T_m = 66 °C. Es scheint außerdem so, als ob auf diesem Wege niedrige Verzweigungsgrade und damit hohe Schmelzpunkte nur auf Kosten eingeschränkter Molekulargewichte der Polymere erlangt werden können.

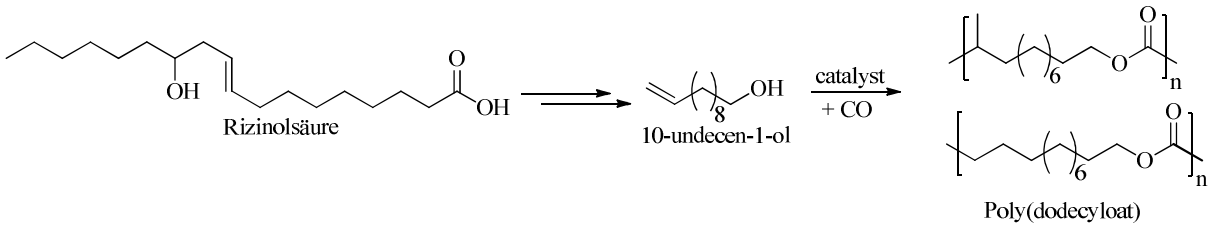


Abbildung 8.1 Bildung von Poly(dodecyloat) aus Rizinolsäure.

Um Fettsäureester vollständig für die Herstellung von auf nachwachsenden Rohstoffen basierenden Polymeren nutzen zu können müssen diese an beiden Kettenenden funktionelle Gruppen tragen. Bei ungesättigten Fettsäureestern befindet sich die Doppelbindung jedoch innerhalb der Molekülkette. In Gegenwart katalytischer Mengen $Pd(OAc)_2$, 1,2-bis[(di-*tert*-butylphosphino)methyl]benzol und Methanesulfonsäure lassen sich interne Olefine durch eine Alkoxycarbonylierungsreaktion selektiv zum endständigen Ester umsetzen. Die isomerisierende Alkoxycarbonylierung von Methyloleat und Ethylerucat lieferte jeweils Dimethyl-1,19-nonadecanedioat und Diethyl-1,23-tricosanedioate in einer Reinheit von > 99 %.

Die so erhaltenen, linearen, langkettigen Dicarbonsäureester wurden einerseits durch Reduktion mit $LiAlH_4$ und andererseits über eine durch einen Dichlorbis[2-(diphenyl phosphino)ethylamin]rutheniumkomplex katalysierte Hydrierung zu den entsprechenden Diolen umgesetzt. In beiden Fällen wurden die gewünschten, langkettigen Diole in Reinheiten von > 99 % erhalten.

Polykondensation von Dimethyl-1,19-nonadecandioat mit Nonadecan-1,19-diol lieferte das neuartige Poly(1,19-nonadecadiyl-1,19-nonadecandioat) mit einem Molekulargewicht von üblicherweise M_w = 2 × 10^4 g mol^{-1}, einer Schmelztemperatur von T_m = 103 °C, einer Kristallisationstemperatur von T_c = 87 °C, einer Schmelzenthalpie von ΔH_m = 140 J g^{-1} und einer Kristallinität von circa 70 %. Poly(1,23-tricosadiyl-1,23-triosandioat) aus dem linearen C_{23} Diester und Diol wurde ebenfalls mit einem Molekulargewicht von M_w = 2 × 10^4 g mol^{-1}, einer Schmelztemperatur von T_m = 99 °C, einer Kristallisationstemperatur T_c = 84 °C, einer relativ hohen Schmelzenthalpie von ΔH_m = 180 J g^{-1} und einer Kristallinität von circa 75 % erhalten.

Das durch Alkoxycarbonylierung von Ethylerucat erhaltene Diethyl-1,23-tricosandioat wurde des Weiteren durch Hydrolyse in die entsprechende Dicarbonsäure und in einer vierstufigen Reaktion in das entsprechende Diamin umgewandelt. Aus der so erhaltenen C_{23} Dicarbonsäure und der kommerziell erhältlichen C_{19} Dicarbonsäure sowie dem C_{23} Diamin und den kommerziell erhältlichen C_{11} und C_{12} Diaminen wurden die neuen Polyamide PA 11 19, PA 11 23, PA 12 19, PA 12 23, PA 23 19 und PA 23 23 hergestellt (Abbildung 8.2).

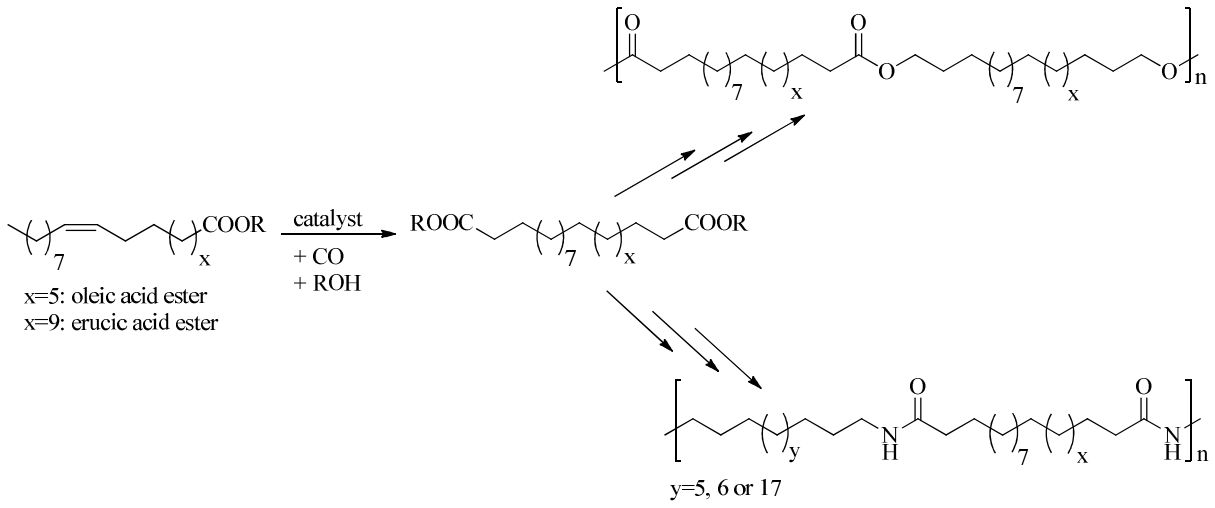


Abbildung 8.2 Bildung von Polyestern und Polyamiden aus Öl- und Erucasäureestern.

Diese Polyamide wurden mit Molekulargewichten von circa M_n = 10^4 g mol^{-1} erhalten. Die Polyamide PA 23 19 und PA 23 23 aus Tricosan-1,23-diamine zeigen Schmelztemperaturen von T_m = 156 °C und T_m = 152 °C. Die Polyamide PA 11 19, PA 11 23, PA 12 19 und PA 12 23 aus dem kürzerkettigeren Diamino-1,11-undecan und Diamino-1,12-dodecan weisen erwartungsgemäss höhere Schmelzpunkte zwischen T_m = 167 °C und T_m = 169 °C auf.

Der oben beschriebene Ansatz erlaubt die gut funktionierende und vollständige Nutzung der in Fettsäuren enthaltenen langen Kohlenwasserstoffketten bei der Herstellung teilkristalliner Polyester und Polymide.

Dieser vollständige, lineare Einbau ist für das Erreichen beträchtlich höherer Schmelzpunkte bei Polyestern sehr vorteilhaft. In aliphatischen Polyamiden führen die langen Kohlenwasserstoffketten zu bedeutend niedrigeren Schmelztemperaturen als die der derzeit industriell etablierten aliphatischen Polyamide. Mit zunehmenden aliphatischen Anteilen in Polykondensaten nähern sich deren Schmelzpunkte im Allgemeinen dem von Polyethylen an, da der Einfluss funktioneller Gruppen, wie die Behinderung der Kristallisation durch Estergruppen oder die erhöhte Wechselwirkung einzelner Ketten untereinander durch Wasserstoffbrückenbindungen, abnimmt.

Alle Arten von Reaktionen, wie z.B. die Carbonylierungs-,[29] Reduktions- und Polycondensationsreaktion[63, 111], welche in dieser Arbeit für die Herstellung von Polymeren aus nachwachsenden Rohstoffen verwendet wurden, sind Reaktionen, die großtechnisch sehr bewährt sind.

9 Experimental Section

9.1 Materials and General Considerations

Unless noted otherwise, all manipulations were carried out under an inert gas atmosphere using standard glovebox or Schlenk techniques. Ethanol and methanol were distilled from magnesium turnings/iodine, THF from sodium/benzophenone, pyridine from CaH_2, and toluene from sodium under argon prior to use. All other solvents were utilised in technical grade as received. 10-undecen-1-ol was supplied by ACME Synthetic Chemicals (Mumbai, India), methyl oleate (99 %), dodecane-1,12-diamine, methanesulfonylchloride, triethylamine, sodium azide, sodium methanolate, palladium on charcoal (3 wt.-%), *tert*-butylchloride, phosphorous trichloride, titanium(IV)butoxide, 1,3-dichloropropane, acetylacetone and methanesulfonic acid (98 %) by Sigma Aldrich, methyl oleate (75 %), methyl erucate (90 %), 1,2-bis[(di-*tert*-butylphosphino)methyl]benzene (98 %) and 2-(diphenyl phosphino)ethylamine by ABCR, ethyl erucate (95 %), nonadecane-1,19-dicarboxylic acid and undecane-1,11-diamine by TCI. $Pd(II)Cl_2$ and magnesium turnings were supplied by Merck, $LiAlH_4$ and *tert*-butyllithium (1.6 M in pentane) by Acros, carbon monoxide (3.7 grade) and hydrogen (5.0 grade) were supplied by Air Liquide. 1,3-diphosphinopropane[144] was available in the group and was synthesised according to published procedures. All materials were used as received unless noted otherwise.

NMR spectra were recorded on a Bruker Avance III 400 instrument, on a Varian Unity INOVA 400 instrument, on a Bruker Avance III 600 instrument equipped with a Cryo Probe Triple resonance CPTCI, or on a Bruker AC 250 instrument. ^{1}H and ^{13}C NMR chemical shifts were referenced to the solvent signal. ^{1}H and ^{13}C NMR assignments are supported by COSY, phase sensitive HSQC and HMBC experiments. Elemental analyses were performed up to 950 °C on an Elementar Vario EL instrument. Gas chromatography was carried out on an Agilent Technologies 7890A GC system equipped with a Phenomenex ZB-5 ms w/Guardian capillary column (30m × 0.25 mm × 0.25 μm) using mass (Agilent Technologies 5975C inert MSD with triple-axis detector) and flame-ionisation detection. Helium of 99.995 % purity was used as the carrier gas and the inlet temperature was 250 °C. The initial temperature of 50 °C was kept for 1 min, after which the column was heated at a rate of 30 K min^{-1} up to 280 °C. The final temperature was kept for 8 min. Gas chromatography was also carried out

on a Perkin Elmer Clarus 500 GC system equipped with an auto sampler and a Perkin Elmer Elite-5 capillary column (30m × 0.25 mm × 0.25 μm) using flame-ionisation detection. Helium of 99.995 % purity was used as the carrier gas and the inlet temperature was 300 °C. The initial temperature of 90 °C was kept for 1 min, after which the column was heated at a rate of 30 K min^{-1} up to 280 °C. The final temperature was kept for 8 min. Differential scanning calorimetry (DSC) was performed on a Netzsch Phoenix 204 F1 instrument at a heating/cooling rate of 10 K min^{-1}. DSC data reported are from second heating cycles. Gel permeation chromatography (GPC) was 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. Data reported were determined via direct calibration with linear polyethylene standards (refractive index detector). Polymer samples which were soluble in THF were measured on a Polymer Laboratories PL-GPC 50 with two PLgel 5 μm MIXED-C columns and a RI-detector in THF at 40 °C vs. polystyrene standards. Wide angle X-Ray diffraction was performed on a Bruker AXS D8 Advance diffractometer using $CuK_{\alpha 1}$ radiation. Diffraction patterns were recorded in the range 10 to 60 degrees 2Θ, at temperatures of 25° and 120°. The crystallinity was estimated with a deconvolution fitting routine as the ratio between the area corresponding to the crystalline reflections and the total area of the WAXS pattern (cf. Figure 3.2). Position and shape of the amorphous halo were determined from the diffraction pattern of the melt at 120°C.

9.2 Preparation of Di-*tert*-butylchlorophosphine

Di-*tert*-butylchlorophosphine was prepared analogous to a previously reported procedure.[145] Dry magnesium turnings (4.0 mol) were weighed into a 2 L three-necked flask equipped with a reflux condenser, an addition funnel and a large magnetic stirring bar and were covered with 200 mL diethyl ether. *Tert*-butylchloride (4.0 mol) was transferred into the addition funnel. For initiation of the Grignard reaction ca. 25 mL *tert*-butylchloride were added. The remaining *tert*-butylchloride was diluted with 200 mL diethyl ether and slowly added at a rate that caused light reflux of the solvent. After complete addition the reaction mixture was refluxed for 1 hour. Then the grey suspension was filtrated over a D_3 frit and the residual solid was washed with diethyl ether. The concentration of the solution was determined by back titration. For this purpose 10 mL of 0.1 M HCl were added to 0.1 mL of the Grignard solution which was then titrated with 0.1 M NaOH. Yield: 1320 mL of a 1.15 M *tert*-butylmagnesium chloride solution (1.5 mol).

A 4 L three-necked flask equipped with a reflux condenser, an addition funnel and an overhead stirrer was charged with the *tert*-butylmagnesium chloride solution. At -40 °C (isopropanol/dry ice) PCl_3 (0.75 mol) in 950 mL diethyl ether was slowly added via the addition funnel. After complete addition the reaction mixture was allowed to warm to room temperature and was then refluxed for 30 minutes. To facilitate the removal of $MgCl_2$ 300 mL dioxane were added and the mixture was refluxed for another 1.5 hours. After cooling to room temperature the reaction mixture was filtrated through a frit to separate the ethereal solution from solid residues. The diethyl ether was then removed under atmospheric pressure. Distillation of the residue under reduced pressure at 110°C / 88 mbar yielded 49.1 g (36 %) di-*tert*-butylchlorophosphine as a colourless liquid. ^{1}H and ^{31}P spectra agree with previously reported data.[145]

9.3 Preparation of Di-*tert*-butylphosphine

A solution of di-*tert*-butylchlorophosphine (0.16 mol) in 130 mL diethyl ether was added drop wise to a suspension of $LiAlH_4$ (0.17 mol) in 250 mL diethyl ether. The reaction mixture was stirred over night at room temperature. Excess $LiAlH_4$ was quenched by slowly adding 15 mL methanol. Then 15 mL saturated NH_4Cl solution and 40 mL 2N HCl were added and vigorously stirred. After phase separation the etheral phase was cannula-transferred into a Schlenk, the remaining water phase was extracted three times with 20 mL diethyl ether. Distillation under reduced pressure at 37 °C / 15 mbar yielded 17.1 g (73 %) di-*tert*-butylphosphine as a colourless liquid. ^{1}H and ^{31}P spectra agree with previously reported data.[146]

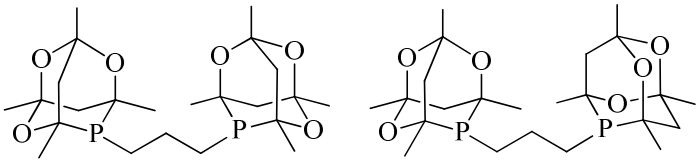
9.4 Preparation of 1,3-Bis(di-*tert*-butylphosphino)propane (dtbpp)

1,3-Bis(di-*tert*-butylphosphino)propane was prepared following a literature procedure.[147] To a stirred solution of di-*tert*-butylphosphine (103 mmol) in 110 mL diethyl ether *tert*-butyllithium (76 mL of a 1.6 M solution in pentane) was added drop wise over a period of 5-10 minutes at 0 °C. The solution turned pale yellow and 1,3-dichloropropane (53 mmol) was added directly. The reaction mixture was stirred for another 20 minutes at 0 °C and was then allowed to warm to room temperature and stir for 1 hour. A gradual formation of a white precipitate was noted. After removal of the solvent in vacuum, 40 mL hexane and 75 mL degassed water were added. The organic phase was cannulated off and the aqueous phase was extracted with hexane (3 × 40 mL). The solvent was removed in vacuum from the combined

organic layers. Kugelrohrdistillation at 150 °C / 1.6 × 10^{-1} yielded 11.4 g (64 %) 1,3-bis(di-*tert*-butylphosphino)propane as a colourless, viscous liquid. ^{1}H and ^{31}P spectra agree with previously reported data.

9.5 Preparation of 1,3-Bis(trioxa-adamantylphosphino)propane

1,3-bis(trioxa-adamantylphosphino)propane was prepared following a literature procedure.[148] To a stirred mixture of acetylacetone (57 mmol) and 20 mL 5 M aqueous HCl 1,3-diphosphinopropane (9.3 mmol) was added drop wise over a period of 5-10 minutes. The formation of a white precipitate was observed. The resulting mixture was stirred at room temperature for a week. Then the white precipitate was separated from the mixture by filtration over a Buchner funnel and was thoroughly washed with water. After drying in vacuum the desired diphosphine was obtained as a mixture of diastereoisomers in 37 % (1.6 g) yield.



9.6 Preparation of Tetrachlorobis(tetrahydrofuran)hafnium(IV)

Tetrachlorobis(tetrahydrofuran)hafnium(IV) was prepared following a literature procedure.[149] To a stirred mixture of hafniumtetrachloride (2.7 mmol) and 10 mL dichloromethane tetrahydrofuran (10.6 mmol) was slowly added. Under slight pinking of the solution the hafniumtetrachloride dissolved. The thus obtained solution was stirred for 1 hour until the formation of a white precipitate was observed. The white precipitate was separated from the mixture and repeatedly washed with pentane. The filtrate was cooled in a isopropanol/dry ice cooling bath for 30 minutes until the formation of further white precipitate was observed. The precipitate was again separated from the mixture and repeatedly washed with pentane. This procedure was repeted until no further formation of precipitated was observed. After drying in vacuum the desired product was obtained in 67 % (0.82 g) yield.

9.7 Preparation of Poly(dodecyloate) by Tetrachlorobis(tetrahydrofuran)hafnium(IV) catalysis from 12-hydroxydodecanoic acid

The polymerisation of 12-hydroxydodecanoic acid was carried out analogous to a reported procedure.[150] 12-hydroxydodecanoic acid (116 mmol) in 20 mL m-xylene was refluxed over an addition funnel filled with 4 Å molecular sieves until the reaction mixture solidified. The solidified reaction mixture was then heated to 150 °C under vacuum for 12 hours.[151] The obtained polymer was dissolved in dichloromethane and precipitated from methanol and dried in vacuum at 50 °C.

9.8 Carbonylation Polymerisation of 10-Undecen-1-ol

9.8.1 General Procedure A - Cobalt-catalysed

Carbonylation polymerisations were carried out in a 280 mL stainless steel mechanically stirred (1500 rpm) pressure reactor equipped with a heating/cooling jacket controlled by a thermocouple dipping into the polymerisation mixture and a glass inlay. For detailed reaction conditions see Table 3.1. Prior to a polymerisation experiment the reactor was purged several times with argon. $[Co_2(CO)_8]$ or $[Co_4(CO)_{12}]$, respectively, were weighed into a dry Schlenk tube in the glovebox. Pyridine and 10-undecen-1-ol were added using standard Schlenk techniques. The mixture was stirred until the $[Co_2(CO)_8]$ or $[Co_4(CO)_{12}]$, respectively, dissolved. The reaction mixture was cannula-transferred into the reactor in an argon counter stream. The reactor was closed, pressurised with carbon monoxide, and heated to the desired reaction temperature (pressures given in Table 3.1 refer to pressure at reaction temperature). After the desired reaction time the reactor was rapidly cooled to room temperature, and vented. The solid polymer was recovered from the reactor, dissolved in dichloromethane, and precipitated from methanol. The polymer was isolated by filtration, washed several times with methanol and dried in vacuum at 50 °C.

9.8.2 Removal of Residual Cobalt

For NMR analysis residual cobalt was removed, as paramagnetic impurities can impact the quality of the NMR spectra. For this purpose 2 g of polymer were dissolved in 50 mL of dichloromethane. To this polymer solution were added 50 mL 0.1 M aqueous EDTA (ethylenediaminetetraacetate disodiumsalt) solution, 1 mL 30 % H_2O_2, and 0.5 mL 37 %

aqueous HCl. The mixture was stirred well for one day at room temperature. The pink aqueous phase formed was separated, and the polymer was precipitated from methanol, isolated by filtration, washed thoroughly with methanol, and finally dried in vacuo at 50 °C. For acquisition of ^{13}C-NMR spectra, a small amount of [$Cr(acac)_3$] was added. As an alternative or in addition to this procedure, CS_2 can be added to mask cobalt traces if required.

9.8.3 General Procedure B - Palladium-catalysed

Carbonylation polymerisations were carried out in a 280 mL stainless steel mechanically stirred (500 rpm) pressure reactor equipped with a heating/cooling jacket controlled by a thermocouple dipping into the polymerisation mixture. For detailed reaction conditions see Table 3.2. Prior to a polymerisation experiment the reactor was purged several times with argon. $Pd(OAc)_2$ was weighed under air into a dry Schlenk tube equipped with a magnetic stirring bar. When applying ligands **1** and **2** (Scheme 3.3) the Schlenk tube was purged several times with argon and 2 mL toluene using standard Schlenk techniques were added before introducing the Schlenk tube into the glove box where the phosphine ligand was added. Ligands **3** and **4** (Scheme 3.3) were weighed into the Schlenk tube together with $Pd(OAc)_2$ prior to purging several times with argon. 10-undecen-1-ol, toluene and methanesulfonic acid were added using standard Schlenk techniques. Vigorous stirring afforded a homogenous reaction mixture which was cannula-transferred into the reactor in an argon counter stream. The reactor was closed, pressurised with carbon monoxide and heated to the desired reaction temperature. After the desired reaction time the reactor was rapidly cooled to room temperature, and vented. The solvent was removed in vacuo and the remaining yellow solid was dissolved in a small amount of toluene. Then the polymer was precipitated from methanol, diethyl ether or hexane and dried in vacuum at 50 °C.

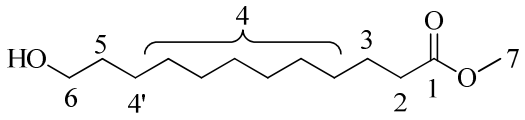
9.9 Methoxycarbonylation of 10-Undecen-1-ol

9.9.1 Palladium - catalysed

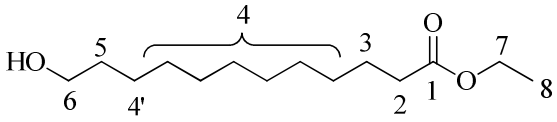
Carbonylations were carried out in a 280 mL stainless steel mechanically stirred (500 rpm) pressure reactor equipped with a heating/cooling jacket controlled by a thermocouple dipping into the polymerisation mixture. For detailed reaction conditions see Table 4.1 and Table 4.2. Prior to a polymerisation experiment the reactor was purged several times with argon. $Pd(OAc)_2$ was weighed under air into a dry Schlenk tube equipped with a magnetic stirring

bar which was then introduced into the glovebox where the dtbox ligand was added. In the case of the dtbpp also 2 mL toluene were added. The Schlenk tube was removed from the glovebox and all other reactants were added using standard Schlenk techniques. Vigorous stirring afforded a homogenous reaction mixture which was cannula-transferred into the reactor in an argon counter stream. The reactor was closed, pressurised with carbon monoxide and heated to the desired reaction temperature. After the desired reaction time the reactor was rapidly cooled to room temperature, and vented. The solvent was removed in vacuo to give the crude product as pale yellow oil.

The composition of the reaction mixtures was determined by ^{1}H-NMR spectroscopic integration of characteristic signals of the species present and subsequent ratio calculation. (For peak assignment confer the respective spectra in section 4 and the appendix).



^{1}H-NMR (400 MHz, $CDCl_3$, RT): δ 3.62 (s, 3H, 7-H), 3.52 (t, $^{3}J_{H-H}$ = 6.5 Hz, 2H, 6-H), 2.25 (t, $^{3}J_{H-H}$ = 7.5 Hz, 2H, 2-H), 1.65-1.47 (m, 4H, 3-H, 5-H), 1.4-1.1 (m, 14H, 4-H, 4'-H). ^{13}C-NMR (100 MHz, $CDCl_3$, RT): δ 174.42 (C-1), 63.13 (C-6), 51.52 (C-7), 34.27 (C-2), 33.17 (C-5), 29.90-29.32 (C-4), 25.41 (C-4'), 24.88 (C-3).



^{1}H-NMR (400 MHz, $CDCl_3$, RT): δ 4.03 (q, $^{3}J_{H-H}$ = 6.97 Hz, 2H, 8-H), 3.58 (t, $^{3}J_{H-H}$ = 6.5 Hz, 2H, 6-H), 2.20 (t, $^{3}J_{H-H}$ = 7.5 Hz, 2H, 2-H), 1.65-1.47 (m, 4H, 3-H, 5-H), 1.4-1.1 (m, 14H, 4-H, 4'-H). ^{13}C-NMR (100 MHz, $CDCl_3$, RT): δ 174.08 (C-1), 62.86 (C-6), 60.25 (C-7), 34.43 (C-2), 32.17 (C-5), 29.70-29.08 (C-4), 25.83 (C-4'), 25.02 (C-3), 14.29 (C-8).

9.9.2 Cobalt - catalysed

Carbonylations were carried out in a 280 mL stainless steel mechanically stirred (1500 rpm) pressure reactor equipped with a heating/cooling jacket controlled by a thermocouple dipping into the polymerisation mixture and a glass inlay. For detailed reaction conditions see Table 4.3. Prior to a polymerisation experiment the reactor was purged several times with argon. [$Co_2(CO)_8$] was weighed into a dry Schlenk tube in the glovebox. Pyridine, methanol or

ethanol respectively and 10-undecen-1-ol were added using standard Schlenk techniques. The mixture was stirred until the [$Co_2(CO)_8$] dissolved. The reaction mixture was cannula-transferred into the reactor in an argon counter stream. The reactor was closed, pressurised with carbon monoxide and heated to the desired reaction temperature (pressures given in Table 4.3 refer to pressure at reaction temperature). After the desired reaction time the reactor was rapidly cooled to room temperature, and vented. Methanol and pyridine were removed in vacuo. For the removal of residual cobalt 50 mL diethyl ether, 50 mL 0.1 M aqueous EDTA solution, 1 mL 30 % H_2O_2, and 0.5 mL 37 % aqueous HCl were added. The mixture was stirred well over night at room temperature. The pink aqueous phase formed was separated and the organic phase was washed with water until the aqueous phase remained colourless. The organic phase was then dried over $MgSO_4$ and the solvent was removed in vacuo to give the crude product as pale yellow oil.

The composition of the reaction mixtures was determined by ^{1}H-NMR spectroscopic integration of characteristic signals of the species present and subsequent ratio calculation. (For peak assignment confer the respective spectra in section 4 and the appendix).

NMR data of the target compounds see section 9.9.1.

9.10 Polycondensation of Methyl-12-hydroxydodecanoate and Ethyl-12-hydroxydodecanoate

The polycondensation reactions were carried out in a 250 mL flat flange reaction vessel with matching five-necked lid equipped with an overhead stirrer, a vacuum tight stirrer guide (JUVO-Normalschliff-Rührverschluss, Juchheim) and a stainless steel stirrer shaft with mixing paddle. This reaction vessel was charged with the crude methyl-12-hydroxydodecanoate, set under vacuum while stirring for approximately one hour to remove volatiles. Then the reactor containing the starting material was purged several times with argon. After heating the inertised methyl-12-hydroxydodecanoate (0.135 mol) or ethyl-12-hydroxydodecanoate respectively to 80 °C $Ti(OBu)_4$ or $Ti(O^iPr)_4$ (2.7 mmol) respectively was added via syringe and the reaction mixture was stirred at 80 °C for 24 hours. In the course of 6 hours the temperature was then raised to 170 °C. The polymer melt was stirred for another eight hours at this temperature under reduced pressure (10^{-3} bar). After cooling a brownish solid was obtained.

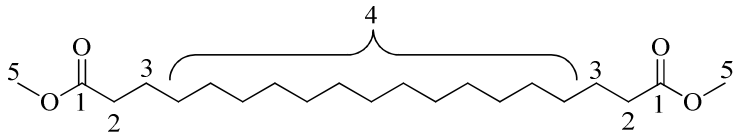
9.11 Carbonylations of Fatty acid esters

9.11.1 General Procedure C

Carbonylations were performed in a 20 mL stainless steel magnetically stirred pressure reactor equipped with a heating jacket and a glass inlay. Prior to a carbonylation experiment the reactor was purged several times with nitrogen. $Pd(OAc)_2$ was weighed under air into a dry Schlenk tube equipped with a magnetic stirring bar which was then introduced into the glovebox where the 1,2-*bis*[(di-tert.-butylphosphino)methyl]benzene (dtbpx) ligand was added. The Schlenk tube was removed from the glovebox and all other reactants were added using standard Schlenk techniques. Vigorous stirring afforded a homogenous reaction mixture which was cannula-transferred into the reactor in a nitrogen counter stream. The reactor was closed, pressurised with 20 bar carbon monoxide and then heated to 90 °C. After 22 hours the reactor was cooled to room temperature and vented.

9.11.1.1 Preparation of Dimethyl-1,19-nonadecanedioate

The carbonylation of methyl oleate in methanol was carried out by the general procedure C described above. For detailed reaction conditions see Table 5.1. After retrieving the reaction mixture from the reactor, methanol was removed in vacuo. The crude product was dissolved in dichloromethane and filtrated over a Büchner funnel. Dichloromethane was removed in vacuo. The obtained dimethyl-1,19-nonadecanedioate was recrystallised from methanol to yield the product in > 99 % purity.

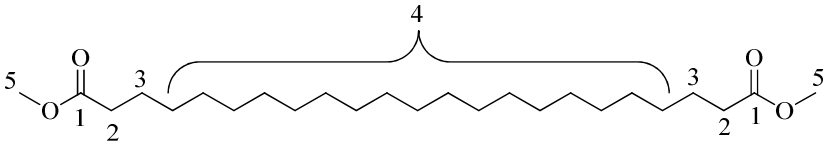


^{1}H-NMR (400 MHz, $CDCl_3$, RT): δ 3.63 (s, 6H, 5-H), 2.27 (t, $^3J_{H-H}$ = 7.5 Hz, 4H, 2-H), 1.63-1.54 (m, 4H, 3-H), 1.31-1.17 (m, 26H, 4-H). ^{13}C-NMR (100 MHz, $CDCl_3$, RT): δ 174.54 (C-1), 51.62 (C-5), 34.32 (C-2), 29.90-29.32 (C-4), 25.16 (C-3).

9.11.1.2 Preparation of Dimethyl-1,23-tricosanedioate

The carbonylation methyl erucate was performed in a 20 mL stainless steel magnetically stirred pressure reactor equipped with a heating jacket and a glass inlay. Prior to the experiment the reactor was purged several times with nitrogen. $Pd(OAc)_2$ (0.11 mmol) was

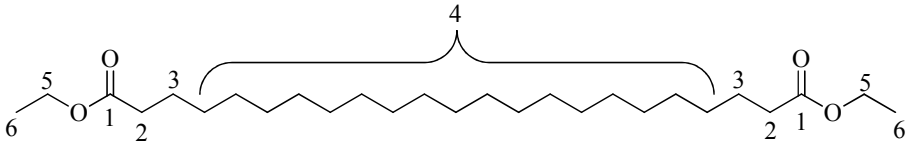
weighed under air into a dry Schlenk tube equipped with a magnetic stirring bar which was then introduced into the glovebox where the 1,2-*bis*[(di-tert.-butylphosphino)methyl]benzene (dtbpx) ligand (0.39 mmol) was added. The Schlenk tube was removed from the glovebox and methyl erucate (5.1 mmol), methanol (0.25 mol, 10 mL) and methanesulfonic acid (0.79 mmol) were added using standard Schlenk techniques. Even vigorous stirring did not afford a homogenous reaction mixture but a two phased system which was cannula-transferred into the reactor in a nitrogen counter stream. The reactor was closed, pressurised with 20 bar carbon monoxide and then heated to 90 °C. After 22 hours the reactor was cooled to room temperature and vented. After retrieving the two phased reaction mixture from the reactor methanol was removed in vacuo. The crude product was dissolved in dichloromethane and filtrated over a Büchner funnel. Dichloromethane was removed in vacuo. The obtained dimethyl-1,23-tricosanedioate was recrystallised from methanol to yield the product in > 99 % purity.



^{1}H-NMR (400 MHz, $CDCl_3$, RT): δ 3.63 (s, 6H, 5-H), 2.27 (t, $^{3}J_{H-H}$ = 7.5 Hz, 4H, 2-H), 1.65-1.54 (m, 4H, 3-H), 1.35-1.17 (m, 34H, 4-H).

9.11.1.3 Preparation of Diethyl-1,23-tricosanedioate

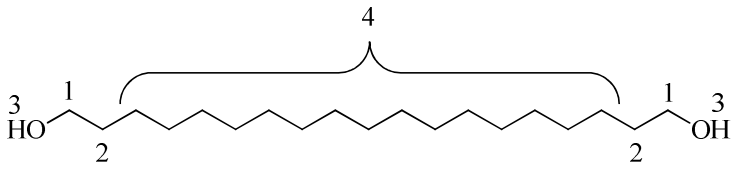
The carbonylation of ethyl erucate in ethanol was carried out by the general procedure C described above. For detailed reaction conditions see Table 5.2. After retrieving the reaction mixture from the reactor ethanol was removed in vacuo. The crude product was dissolved in dichloromethane and filtrated over a Büchner funnel. Dichloromethane was removed in vacuo. The obtained diethyl-1,23-tricosanedioate was recrystallised from ethanol to yield the product in > 99 % purity.



^{1}H-NMR (400 MHz, $CDCl_3$, RT): δ 4.09 (q, $^{3}J_{H-H}$ = 7.2 Hz, 5H, 4-H), 2.25 (t, $^{3}J_{H-H}$ = 7.5 Hz, 4H, 2-H), 1.64-1.53 (m, 4H, 3-H) 1.33-1.16 (m, 40H, 4-H, 6-H). ^{13}C-NMR (100 MHz, $CDCl_3$, RT): δ 174.07 (C-1), 60.3 (C-5), 34.59 (C-2), 29.96-29.30 (C-4), 25.19 (C-3), 14.45 (C-6).

9.12 Preparation of Nonadecane-1,19-diol

Dimethyl-1,19-nonadecanedioate (5.6 mmol) was dissolved in 20 mL THF. This solution was slowly added to a stirred and cooled suspension of $LiAlH_4$ (12.3 mmol) in 40 mL THF. After further addition of 10 mL THF, the stirred mixture was heated to reflux for 1 hour and then stirred over night at room temperature. The reaction was quenched by slowly adding 0.5 mL water, 0.5 mL 15 % aqueous NaOH and 1.5 mL water. The reaction mixture was filtrated at 40 °C over a Buchner funnel. The solvent was removed from the filtrate in vacuo. The resulting nonadecane-1,19-diol was recrystallised from chloroform to yield 1.56 g (93 %) of the pure product.



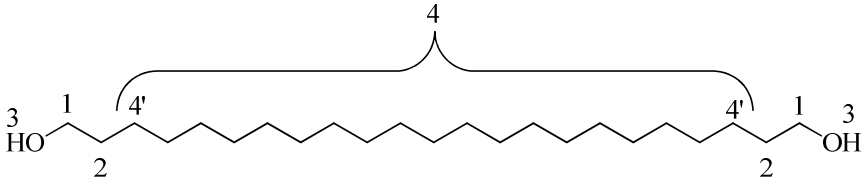
^{1}H-NMR (400 MHz, $C_2D_2Cl_4$, 130 °C): δ 3.68 (t, $^3J_{H-H}$ = 6.5 Hz, 2H, 1-H), 1.7-1.57 (m, 2H, 2-H), 1.49-1.32 (m, 30H, 4-H), 1.13 (br s, 2H, 3-H).

Anal. calcd. for $C_{19}H_{40}O_2$ (M = 300.52 g mol^{-1}): C 75.94, H 13.42. Found: C 76.18, H 13.67.

9.13 Preparation of Tricosane-1-23-diol

9.13.1 Reduction of Diethyl-1,23-tricosanedioate with $LiAlH_4$

Tricosane-1,23-diethylester (5.22 mmol) was dissolved in 20 mL THF. This solution was slowly added to a stirred and cooled suspension of $LiAlH_4$ (13.2 mmol) in 40 mL THF. After further addition of 10 mL THF, the stirred mixture was heated to reflux for 1 hour and then stirred over night at room temperature. The reaction was quenched by slowly adding 0.5 mL water, 0.5 mL 15 % aqueous NaOH and 1.5 mL water. The reaction mixture was filtrated at 40 °C. The solvent was removed from the filtrate in vacuo. The resulting tricosane-1,23-diol was recrystallised from toluene to yield 1.62 g (87 %) of the pure product.



^{1}H-NMR (400 MHz, $C_2D_2Cl_4$, 130 °C): δ 3.67 (t, $^{3}J_{H-H}$ = 6.5 Hz, 2H, 1-H), 1.68-1.58 (m, 2H, 2-H), 1.49-1.32 (m, 38H, 4-H), 1.15 (br s, 2H, 3-H). ^{13}C-NMR (100 MHz, $C_2D_2Cl_4$, 130 °C): δ 63.14 (C-1), 33.14 (C-2), 29.79-29.50 (C-4), 25.99 (C-4').

Anal. calcd. for $C_{23}H_{48}O_2$ (M = 356.63 g mol^{-1}): C 77.46, H 13.57. Found: C 77.58, H 13.60.

9.13.2 Reduction of Diethyl-1,23-tricosanedioate with Dichlorobis[2-(diphenylphosphino) ethylamine]ruthenium

The reduction was carried out, analogous to a reported[109] procedure, 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. Diethyl-1,23-tricosanedioate (5.6 mmol) was weighed under air into a dry Schlenk tube equipped with a magnetic stirring bar which was then purged several times with argon. 20 mL 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 (5.6 μmol) and sodium methanolate (0.56 mmol) were weighed into a second dry Schlenk equipped with a magnetic stirring bar. After removing the Schlenk from the glovebox, 20 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, pressurised with 50 bar hydrogen and then heated to 100 °C. After 22 hours the reactor was cooled to room temperature and vented. After retrieving the reaction mixture from the reactor it was again 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 recrystallised from toluene to obtain 78 % yield.

^{1}H-NMR (400 MHz, $C_2D_2Cl_4$, 130 °C): δ 3.68 (t, $^{3}J_{H-H}$ = 6.5 Hz, 2H, 1-H), 1.68-1.58 (m, 2H, 2-H), 1.49-1.32 (m, 40H, 4-H), 1.25 (br s, 2H, 3-H).

Anal. calcd. for $C_{23}H_{48}O_2$ (M = 356.63 g mol^{-1}): C 77.46, H 13.57. Found: C 76.22, H 13.31.

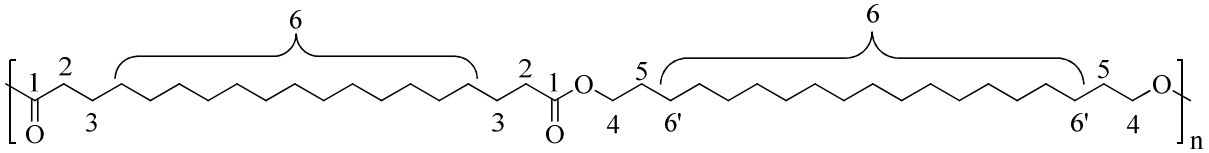
9.13.2.1 Preparation of Dichlorobis[2-(diphenylphosphino)ethylamine]ruthenium

The preparation of Dichloro[2-(diphenylphosphino)ethylamine]ruthenium was prepared analogous to a reported[108] procedure. In the glovebox a round bottomed Schlenk flask, equipped with a magnetic stirring bar, was charged with [$RuCl_2(PPh_3)_3$] (0.436 mmol) and toluene (6 mL). A solution of 2-(diphenylphosphino)ethylamine (0.879 mmol) in toluene (6

mL) was also prepared in the glovebox and transferred into a syringe. After retrieving both solutions from the glovebox the 2-(diphenylphosphino)ethylamine solution was slowly added to the $[RuCl_2(PPh_3)_3]$ solution under vigorous stirring. The obtained dark-brown solution was then heated to 100 °C under Argon for 22 hours. The resulting yellow suspension was cooled to room temperature, introduced into the glovebox and was transferred into a 8 mL screw cap vial under addition of further toluene (4 mL). The suspension was centrifuged and the obtained pale yellow complex was washed several times with toluene until the overlaying solution of the centrifugate was colourless.

9.14 Preparation of Poly(1,19-nonadecadiyl-1,19-nonadecanedioate)

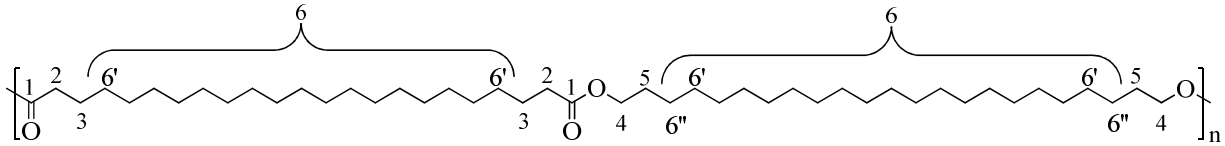
In a 10 ml Schlenk tube dimethyl-1,19-nonadecanedioate (1.4 mmol), nonadecane-1,19-diol (1.4 mmol) and $Ti(OBu)_4$ (0.13 mmol) were heated from 110 °C to 200 °C at 0.01 mbar in the course of 15 hours. After cooling a white solid was obtained.



^{1}H-NMR (400 MHz, $C_2D_2Cl_4$, 130 °C): δ 4.04 (t, $^3J_{H\text{-}H}$ = 6.5 Hz, 4H, 4-H), 2.28 (t, $^3J_{H\text{-}H}$ = 7.3 Hz, 4H, 2-H), 1.69-1.52 (m, 8H, 3-H, 5-H), 1.39-1.18 (m, 56H, 6-H). ^{13}C-NMR (100 MHz, $C_2D_2Cl_4$, 130 °C): δ 174.31 (C-1), 64.70 (C-4), 34.68 (C-2), 30.12-29.42 (C-6), 28.94 (C-5), 26.23 (C-6'), 25.31 (C-3).

9.15 Preparation of Poly(1,23-tricosadiyl-1,23-tricosanedioate)

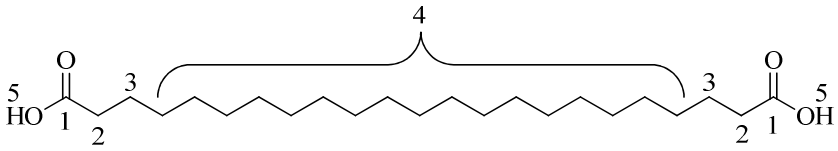
The polymerisation was carried out in a 100 mL two-necked Schlenk tube equipped with an overhead stirrer, a vacuum tight stirrer guide (JUVO-Normalschliff-Rührverschluss, Juchheim), a stainless steel stirrer shaft and a spiral mixing paddle. This Schlenk tube was charged with diethyl-1,23-tricosanedioate (4.49 mmol) and tricosane-1,19-diol (4.49 mmol) and then purged several times with argon. After heating to 110 °C, the obtained melt was stirred for 2 hours. Then $Ti(OBu)_4$ (0.09 mmol) was added and the mixture was stirred for another hour. In the course of 4 hours the temperature was raised to 170 °C. The polymer melt was stirred for one hour at this temperature under reduced pressure, heated to 180 °C and stirred for another hour. After cooling a white solid was obtained.



^{1}H-NMR (400 MHz, $C_2D_2Cl_4$, 130 °C): δ 4.12 (t, $^{3}J_{H-H}$ = 6.5 Hz, 4H, 4-H), 2.33 (t, $^{3}J_{H-H}$ = 7.4 Hz, 4H, 2-H), 1.75-1.63 (m, 8H, 3-H, 5-H), 1.48-1.32 (m, 72H, 6-H). ^{13}C-NMR (100 MHz, $C_2D_2Cl_4$, 130 °C): δ 173.46 (C-1), 64.41 (C-4), 34.6 (C-2), 29.8-29.5 (C-6), 29.32 (C-6'), 29.02 (C-5), 26.14 (C-6''), 25.2 (C-3).

9.16 Preparation of Tricosane-1,23-dicarboxylic acid

In a round bottomed flask KOH (36.3 mmol) was added to a suspension of diethyl-1,23-tricosanedioate (4.5 mmol) in methanol (12 mL). The resulting mixture was refluxed for 2 hours during which more methanol (8 mL) was added. After further addition of KOH (18.9 mmol) the mixture was refluxed for another 8 hours. After cooling the suspension to room temperature the solvent was removed in vacuo. To the obtained white solid water (30 mL) was added. The mixture was acidified to pH = 2 by adding 6N hydrochloric acid. The dicarboxylic acid was filtered off, washed with water and recrystallised from methanol to give a glittery white solid in 96 % yield.



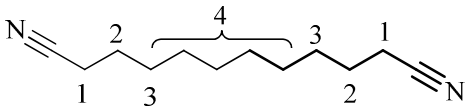
^{1}H-NMR (400 MHz, $C_2D_2Cl_4$, phenol 130 °C): 2.41 (t, $^{3}J_{H-H}$ = 7.4 Hz, 4H, 2-H), 1.78-1.69 (m, 4H, 3-H), 1.49-1.34 (m, 34H, 4-H). ^{13}C-NMR (100 MHz, CD_3OD : $CDCl_3$ = 4 : 3, RT): δ 176.04 (C-1), 34.8 (C-2), 30.53-29.89 (C-4), 25.77 (C-3).

9.17 Preparation of Dodecane-1,12-diamine

9.17.1 Preparation of Dodecane-1,12-dinitrile

Dodecane-1,12-dinitrile was prepared following a literature[128] procedure. Dodecane-1,12-diol (1 mmol) and iodine (6 mmol) were weighed into a 25 mL round bottomed flask. After addition of 7 mL 25 % aqueous ammonia the heterogeneous mixture turned black immediately, probably due to the formation of the explosive nitrogen triiodine. The flask was quickly sealed with an empty balloon fixed to the flask with a cable tie to reduce the escape of ammonia gas from the reaction mixture. The mixture was stirred at 60 °C for 24 hours and

then quenched by addition of water (20 mL) and saturated aqueous Na_2SO_4 solution (6 mL) at 0°C before it was extracted with diethyl ether (3 × 20 mL). The organic layer was washed with brine and dried over sodium sulphate to provide the desired dodecane-1,12-dinitrile in 79 % yield.



^{1}H-NMR (400 MHz, $CDCl_3$, RT): δ 2.29 (t, $^3J_{H-H}$ = 7.1 Hz, 4H, 1-H), 1.64-1.55 (m, 4H, 2-H), 1.44-1.34 (m, 4H, 3-H), 1.30-1.21 (m, 8H, 4-H).

9.17.2 Reduction of Dodecane-1,12 dinitrile to Dodecane-1,12-diamine

Dodecane-1,12-dinitrile (0.79 mmol) was dissolved in 2 mL diethylether. This solution was slowly added to a stirred and cooled suspension of $LiAlH_4$ (1 mmol) in 3 mL diethylether. Then the stirred mixture was heated to reflux for 1 hour. The reaction was quenched by slowly adding 0.04 mL water, 0.04 mL 15 % aqueous NaOH and 0.11 mL water. Unfortunately the dodecane-1,12-diamine as insoluble in diethylether. Therefore the solvent was removed in vacuo and was then replaced by 5 mL THF. The reaction mixture was filtrated at 40 °C to remove the inorganic salts. The solvent was removed from the filtrate in vacuo to give the crude dodecane-1,12-diamine as an off-white solid in 51 % yield. The ^{1}H-NMR spectrum agrees with previously reported data.

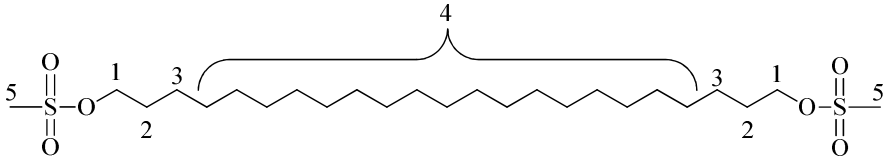
9.18 Preparation of Tricosane-1,23-diamine

Tricosane-1,23-diamine was prepared following a literature[132] procedure by starting from tricosane-1,23-diol and going over tricosane-1,23-dimesylate and tricosane-1,23-diazide.

9.18.1 Preparation of Tricosane-1,23-dimesylate

In a 100 mL two-necked round bottomed flask tricosane-1,23-diol (3.5 mmol) and triethylamine (21 mmol) were dissolved in THF (40 mL) at 50 °C. To this solution mesyl chloride (14 mmol) was slowly added via a syringe. The resulting yellow suspension was stirred for 3 hours until it turned red. After addition of dichloromethane (50 mL) the reaction mixture was successively washed with water (30 mL), 2M HCl (20 mL), water (20 mL), saturated $NaHCO_3$ solution (20 mL) and water (20 mL). The organic phase was dried with

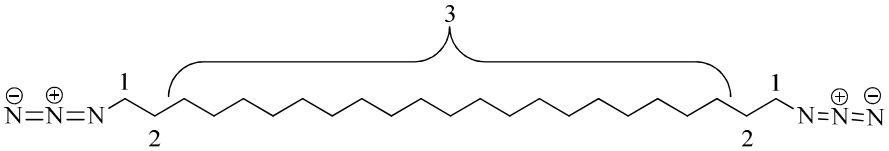
Na_2SO_4 and the solvent was removed in vacuo. After recrystallisation a gleaming white solid was obtained in quantitative yield.



^{1}H-NMR (400 MHz, $CDCl_3$, RT): δ 4.2 (t, $^3J_{H-H}$ = 6.5 Hz, 4H, 1-H), 2.98 (s, 6H, 5-H), 1.77-1.68 (m, 4H, 2-H), 1.42-1.33 (m, 4H, 3-H), 1.33-1.20 (m, 34H, 4-H).

9.18.2 Preparation of Tricosane-1,23-diazide

In a round bottomed flask tricosane-1,23-dimesylate (3.5 mmol) was dissolved in DMF (35 mL) at 80 °C. To this solution sodiumazide (17.5 mmol) was added. The resulting mixture was stirred at 85 °C for 5.5 hours. After cooling the suspension water (10 mL) was added. The DMF-water phase was extracted with hexane twice. The organic layer was succesively washed with saturated $NaHCO_3$ solution (10 mL) and saturated NaCl solution (10 mL). The organic layer was dried with Na_2SO_4 and the solvent was removed in vacuo to give the desired product as a white solid in 79 % yield.

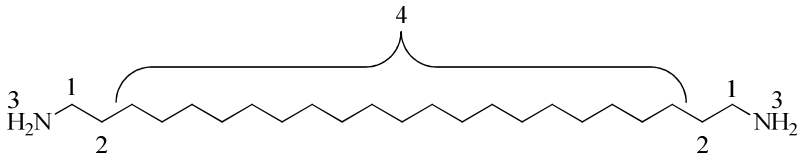


^{1}H-NMR (400 MHz, $CDCl_3$, RT): δ 3.23 (t, $^3J_{H-H}$ = 7 Hz, 4H, 1-H), 1.62-1.52 (m, 4H, 2-H), 1.40-1.18 (m, 38H, 3-H).

9.18.3 Hydrogenation of Tricosane-1,23-diazide to Tricosane-1,23-diamine

Tricosane-1,23-diazide (2.75 mmol) and Pd/C (3 wt.-%) (296 mg, 0.08 mmol Pd) were weighed under air into a dry Schlenk. In an argon counter stream dry and degassed THF (60 mL) was added. The resulting mixture was cannula-transferred into a 280 mL stainless steel mechanically stirred (1500 rpm) pressure reactor equipped with a glas inlay and a heating/cooling jacket controlled by a thermocouple dipping into the reaction mixture which was purged several times with argon prior to the reaction. The reactor was closed and pressurised with 10 bar hydrogen and heated to 40 °C. After 3 hours the reactor was cooled to room temperature, and vented. The reaction mixture was then filtrated repeatedly over a Büchner funnel at 50 °C to remove catalyst residues. Then the solvent was removed in vacuo

to give an off-white solid which was recrystallised from ethanol to give the desired product in 82 % yield.



^{1}H-NMR (400 MHz, dmso-d_6, 130 °C): 2.57 (t, $^{3}J_{H-H}$ = 6.5 Hz, 4H, 1-H), 1.42-1.33 (m, 4H, 2-H), 1.33-1.27 (m, 38H, 4-H).

Anal. calcd. for $C_{23}H_{50}N_2$ (M = 354.66 g mol^{-1}): C 77.89, H 14.21, N 7.90. Found: C 72.57, H 12.74, N 7.00.

9.19 General Procedure for the preparation of Polyamides from Amines and Carboxylic acids

Prior to all polymerisation reactions the so called "nylon salts", the diamine salts of the corresponding dicarboxylic acids, were prepared to ensure an exact stoichiometry of these two components. For this purpose a 10 % ethanolic solution of the diamine was slowly added to an equimolar 10 % ethanolic solution of the dicarboxylic acid at elevated temperature which lead to precipitation of a white solid. This mixture was refluxed for 0.5 to 1.5 hours. After cooling the suspension to room temperature the white solid was filtered off, washed with warm ethanol and dried in vacuo.

Table 9.1 Reaction conditions in polyamide synthesis.

polyamide	excess diamine [mol-%]	T_1 [°C]	T_2 [°C]	time from T_1 to T_2 [h][a]	time at T_2 under argon [h]	time at T_2 under vacuum [h]	colour	$M_n \times 10^4$ (NMR)/ g mol^{-1}
PA 11 19	0	100	250	4	0.5	19	brown	0.4
PA 11 23	0.047	120	210	4.5	3	17	beige	0.5
PA 12 19	0	100	230	0.5	-	72	light brown	1.0
PA 12 23	0.038	100	200	5.5	16.5	4	beige	1.1
PA 23 19	0	100	230	4.5	1.25	16.5	brown	0.9
PA 23 23	0.036	120	210	3	1.5	17.5	light brown	1.3

[a] under argon.

All polymerisations were carried out in a 100 mL two-necked Schlenk tube equipped with an overhead stirrer, a vacuum tight stirrer guide (JUVO-Normalschliff-Rührverschluss, Juchheim), a stainless steel stirrer shaft and a spiral mixing paddle. This Schlenk tube was

charged with the nylon salt prepared before. In the case of PA 11 23, PA 12 23 and PA 23 23 a small excess of the diamine was added. The Schlenk tube was then purged several times with argon and heated to T_1 and further heated to T_2 under argon according to Table 9.1. After cooling beige to brown solids were obtained.

9.20 Ruthenium - complex catalysed preparation of Polyamides

Following a literature procedure for the formation of aliphatic amides from primary alcohols and amines in toluene by ruthenium complex catalysis, low molecular weight polyamides from dodecane-1,12-diol and dodecane-1,12-diamine were prepared.[140] For this prurpose a 100 mL two-necked Schlenk tube equipped with an overhead stirrer, a vacuum tight stirrer guide (JUVO-Normalschliff-Rührverschluss, Juchheim), a stainless steel stirrer shaft and a spiral mixing paddle, was charged with dodecane-1,12-diamine (5 mmol) and dodecane-1,12-diamine (5 mmol) and then purged several times with argon. Then the Schlenk tube was heated to 100 °C under stirring until the two monomers were completely molten. In the mean time $[RuCl_2(cod)]$ (0.25 mmol) KO^tBu (1 mmol), 1,3-diisopropylimidazoliumchloride (0.25 mmol) and tricyclohexylphosphine (0.25 mmol) were weighed into a second Schlenk tube inside the glovebox. Toluene (2.5 ml) was added and the mixture was stirred at 110 °C for 30 minutes before it was carefully added to the molten monomer mixture. The resulting reaction mixture was heated to 170 °C and stirred for 72 hours. After cooling a black solid was obtained.

10 Appendix

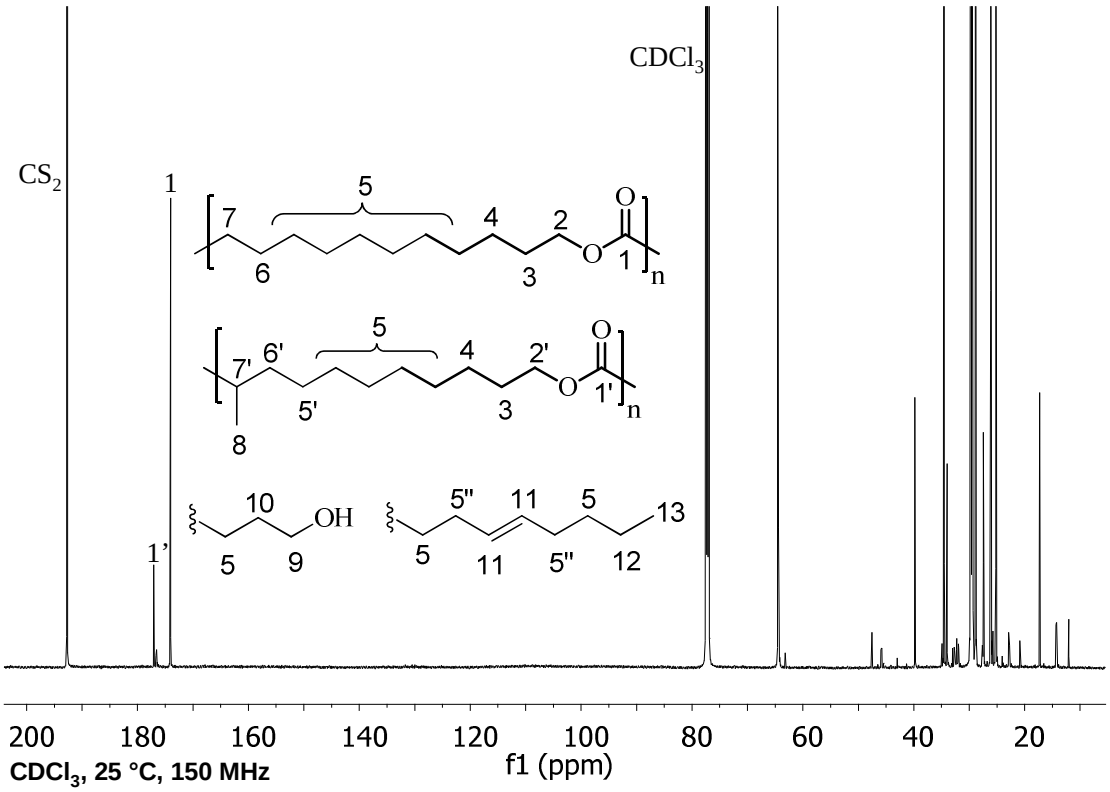


Figure A 1 ^{13}C-NMR spectrum of poly(dodecyloate) prepared with $[Co_2(CO)_8]$/pyridine catalyst.

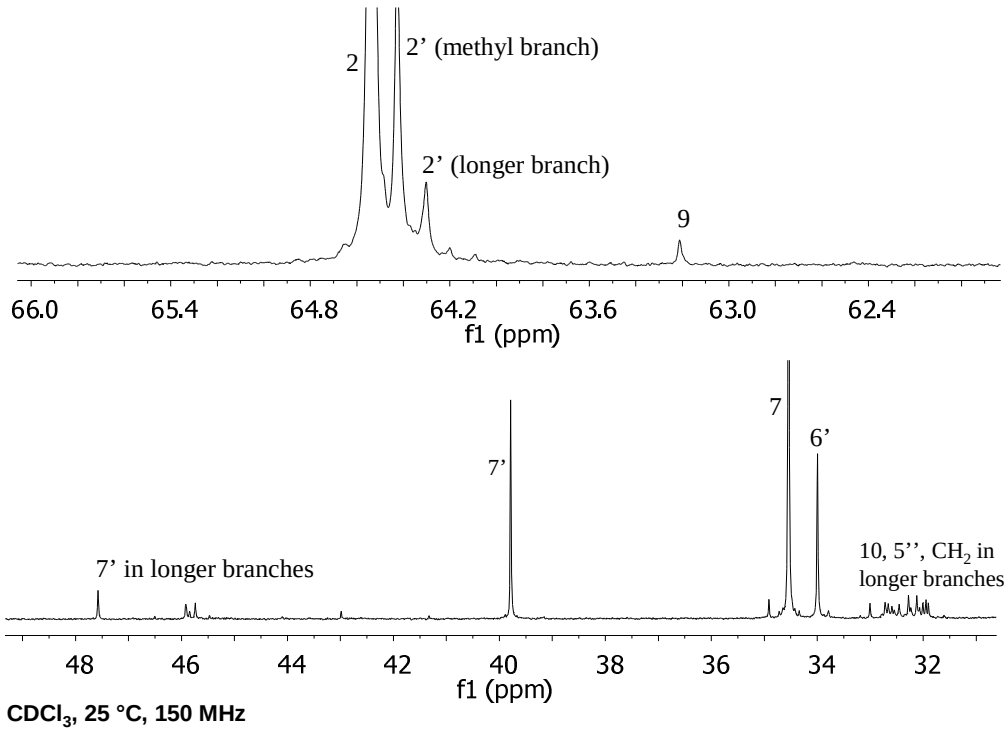


Figure A 2 Details of ^{13}C-NMR spectrum of poly(dodecyloate) prepared with $[Co_2(CO)_8]$/pyridine catalyst.

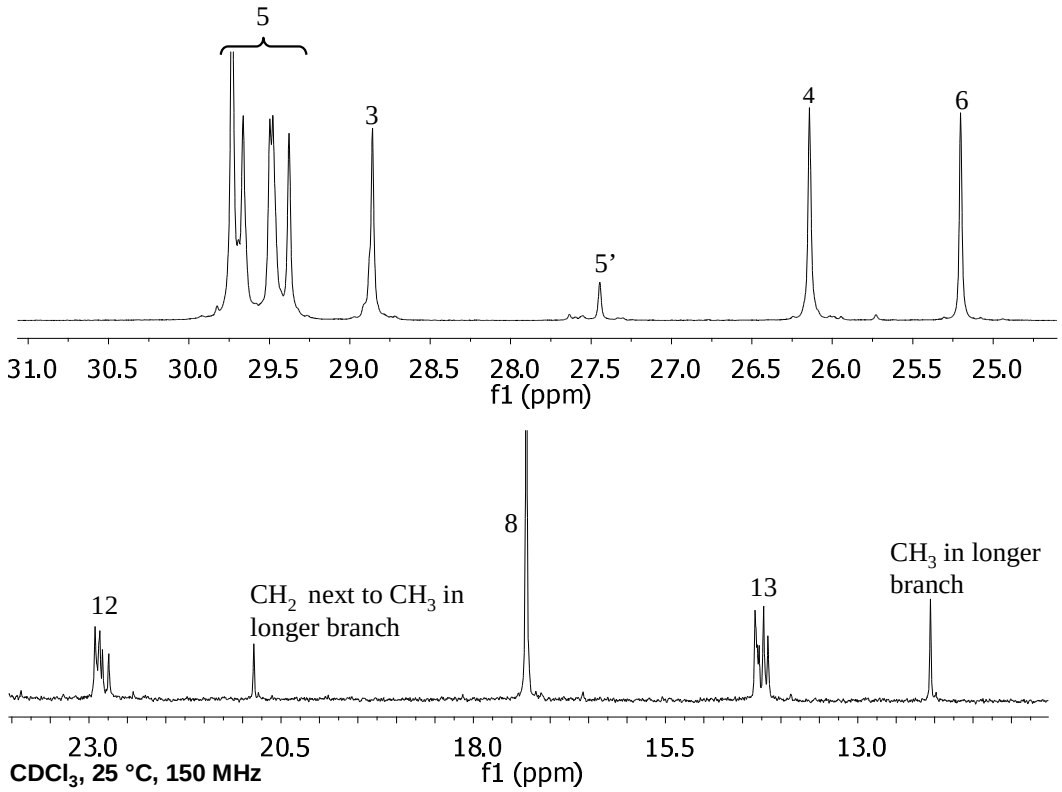


Figure A 3 Details of ^{13}C-NMR spectrum of poly(dodecyloate) prepared with $[Co_2(CO)_8]$/pyridine catalyst.

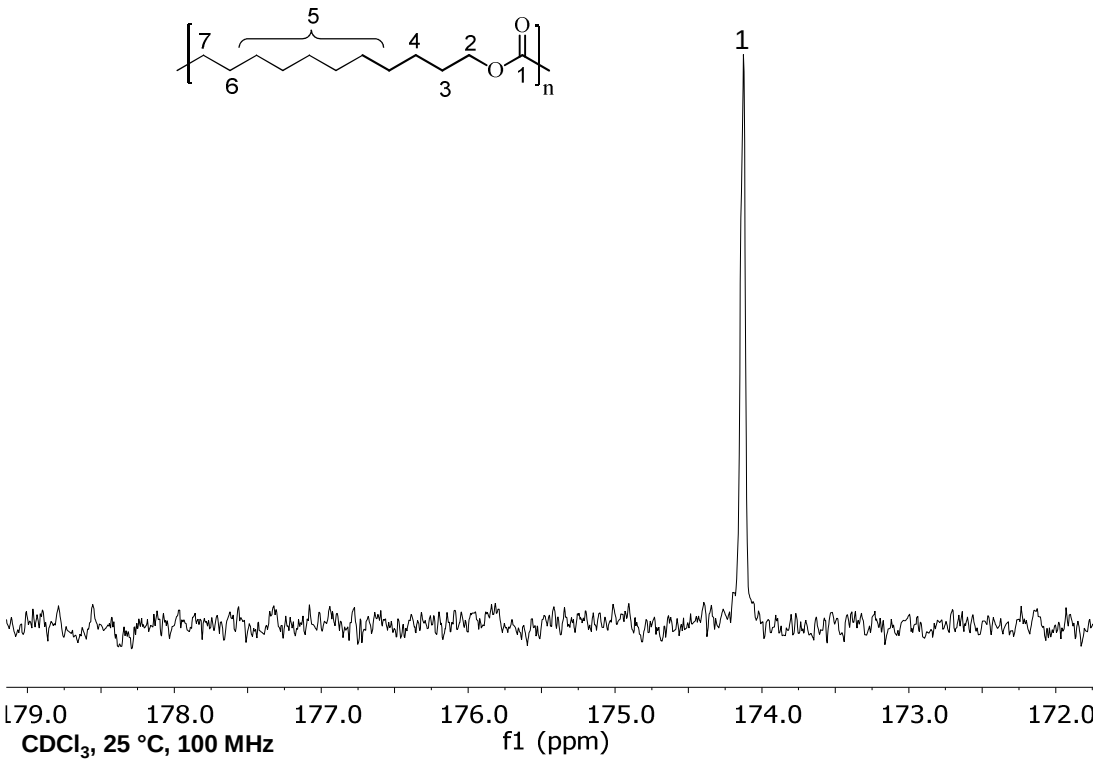


Figure A 4 Carbonyl region of ^{13}C-NMR spectrum of poly(dodecyloate) prepared with Pd(II)/dtbpx catalyst.

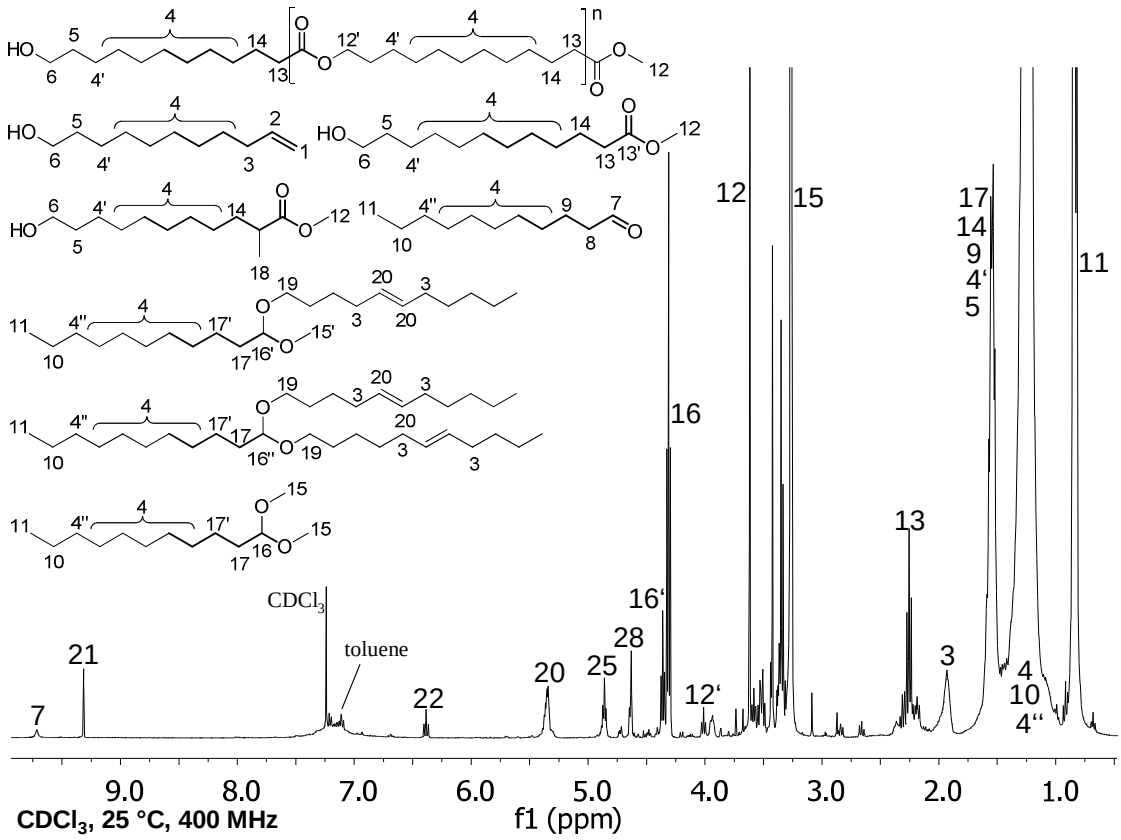


Figure A 5 ^{1}H-NMR spectrum of Pd-catalysed methoxycabonylation of 10-undecen-1-ol with dtbpx ligand (Table 4.2, entry 1).

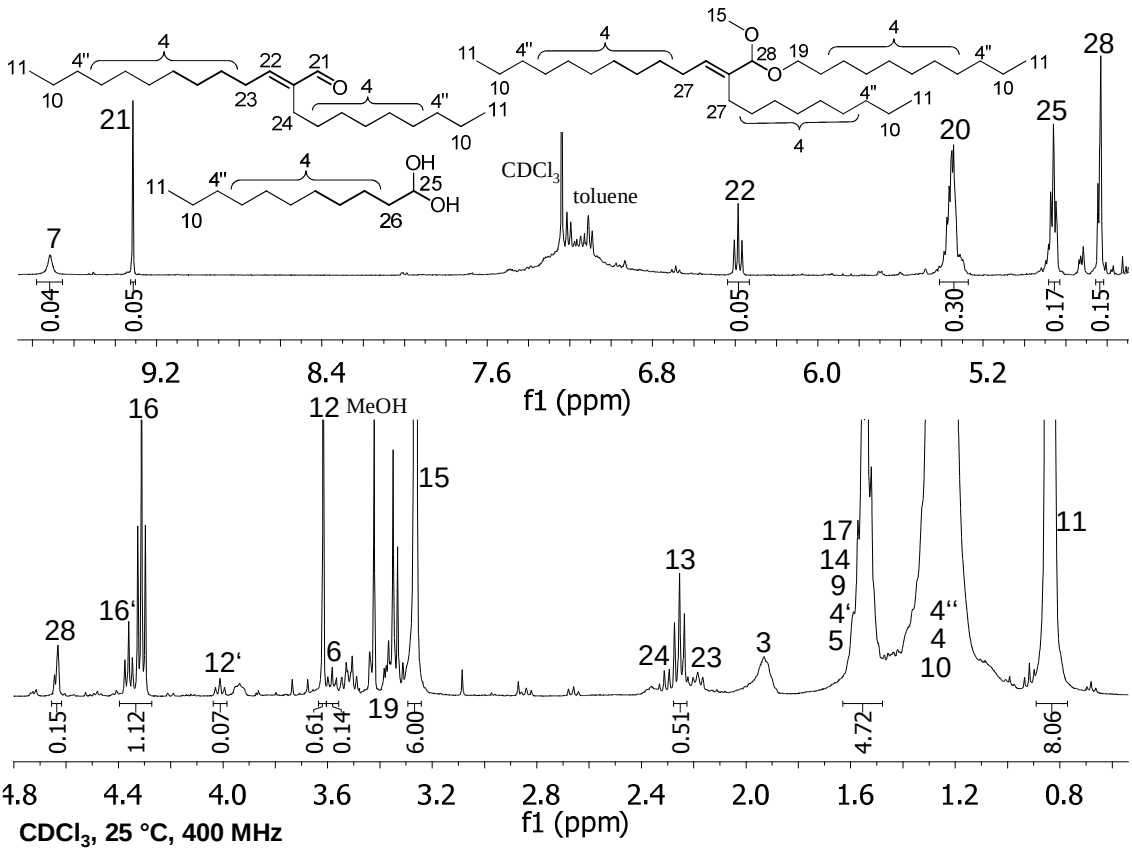


Figure A 6 Details of ^{1}H-NMR of Pd-catalysed methoxycarbonylation of 10-undecen-1-ol with dtbpx ligand.

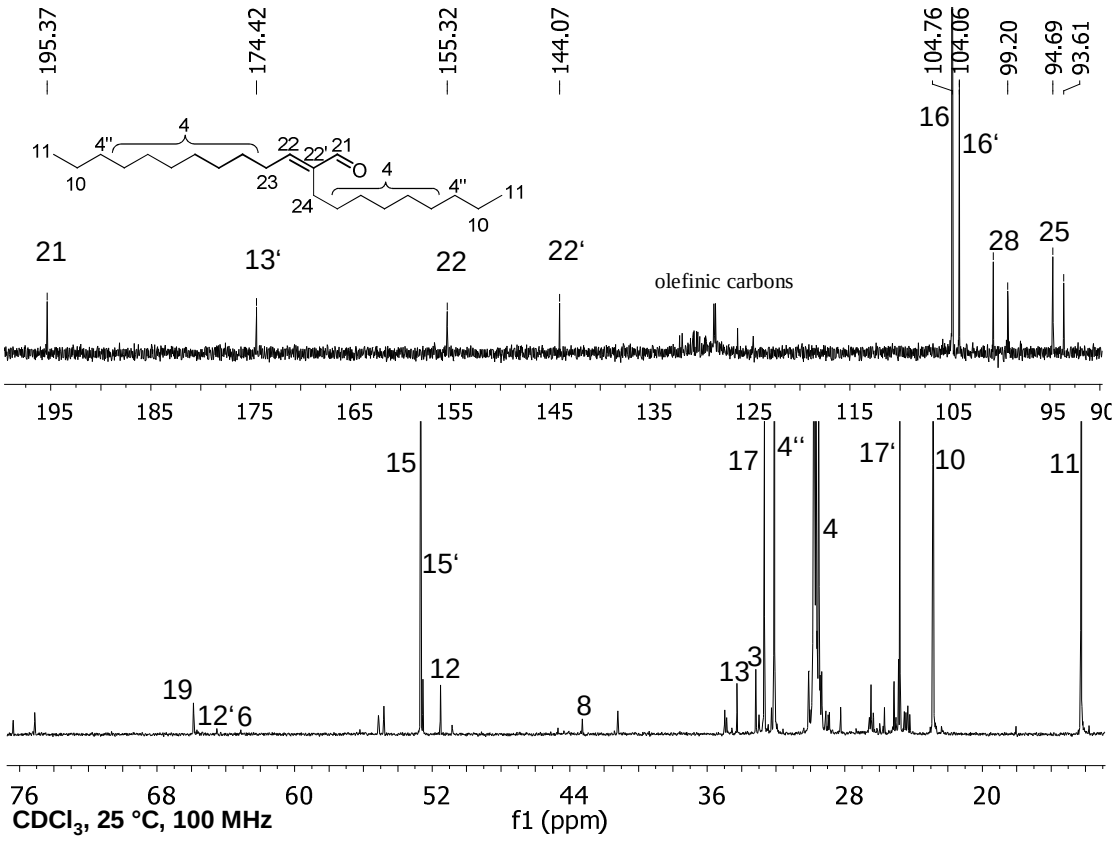


Figure A 7 Detailed ^{13}C-NMR of of Pd-catalysed methoxycarbonylation of 10-undecen-1-ol with dtbpx ligand (Table 4.2, entry 1).

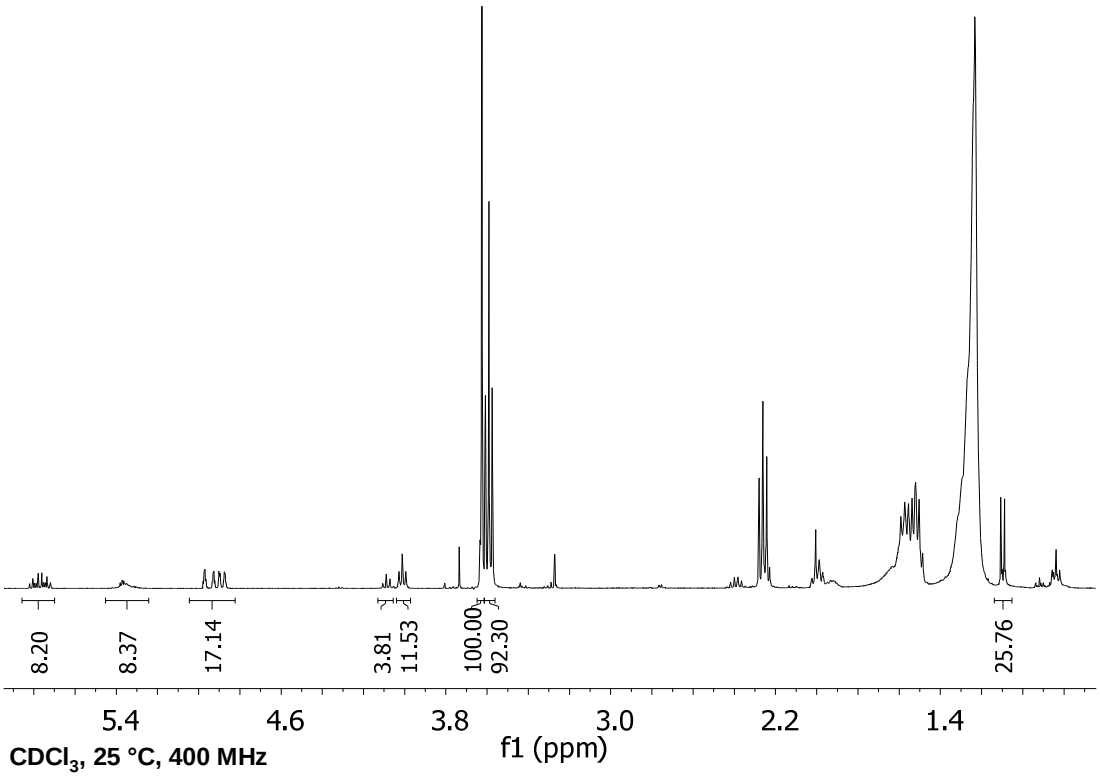


Figure A 8 ^{1}H-NMR spectrum of methyl-12-hydroxydodecanoate (Table 4.3, entry 1).

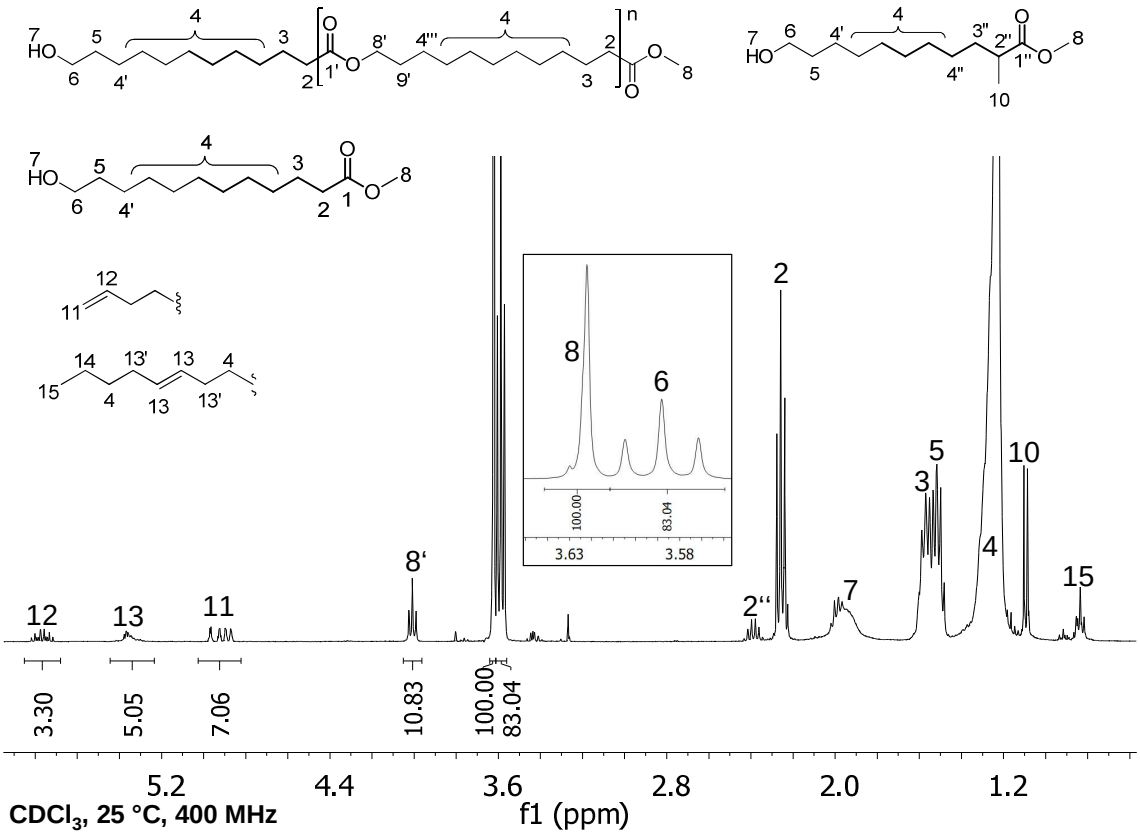


Figure A 9 [1]H-NMR spectrum of methyl-12-hydroxydodecanoate (Table 4.3, entry 2).

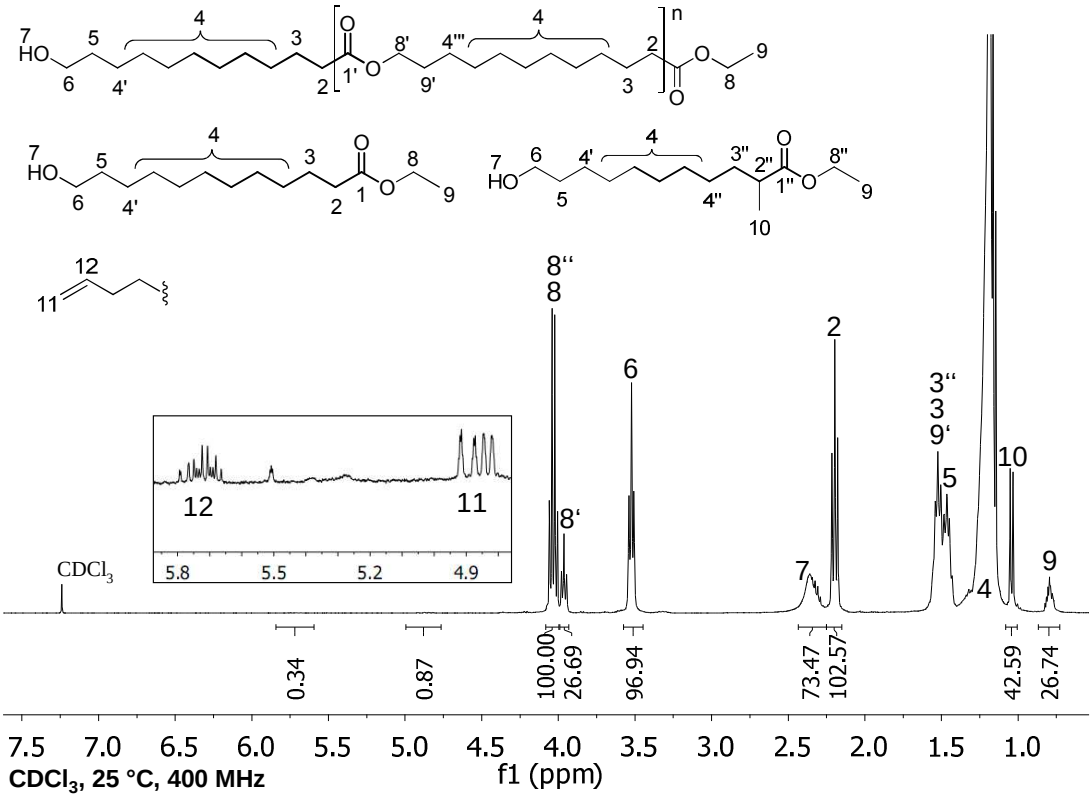


Figure A 10 [1]H-NMR spectrum of ethyl-12-hydroxydodecanoate (Table 4.3, entry 3).

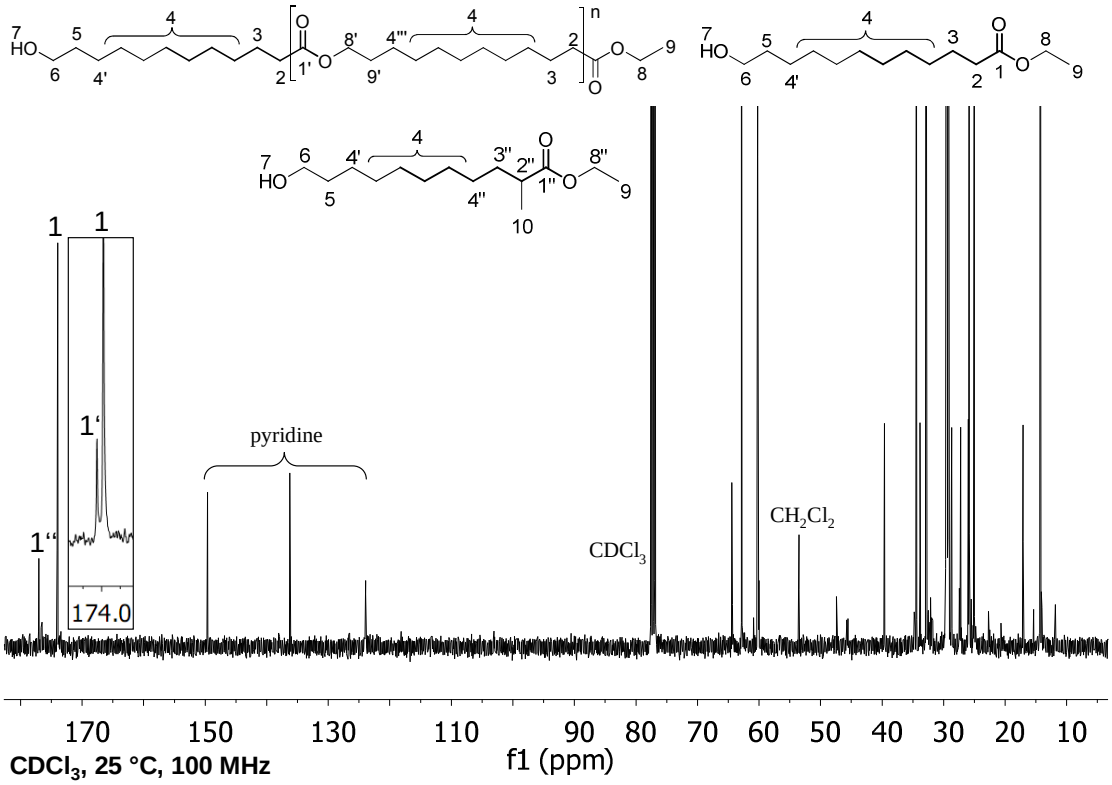


Figure A 11[13]C-NMR spectrum of ethyl-12-hydroxydodecanoate (Table 4.3, entry 4).

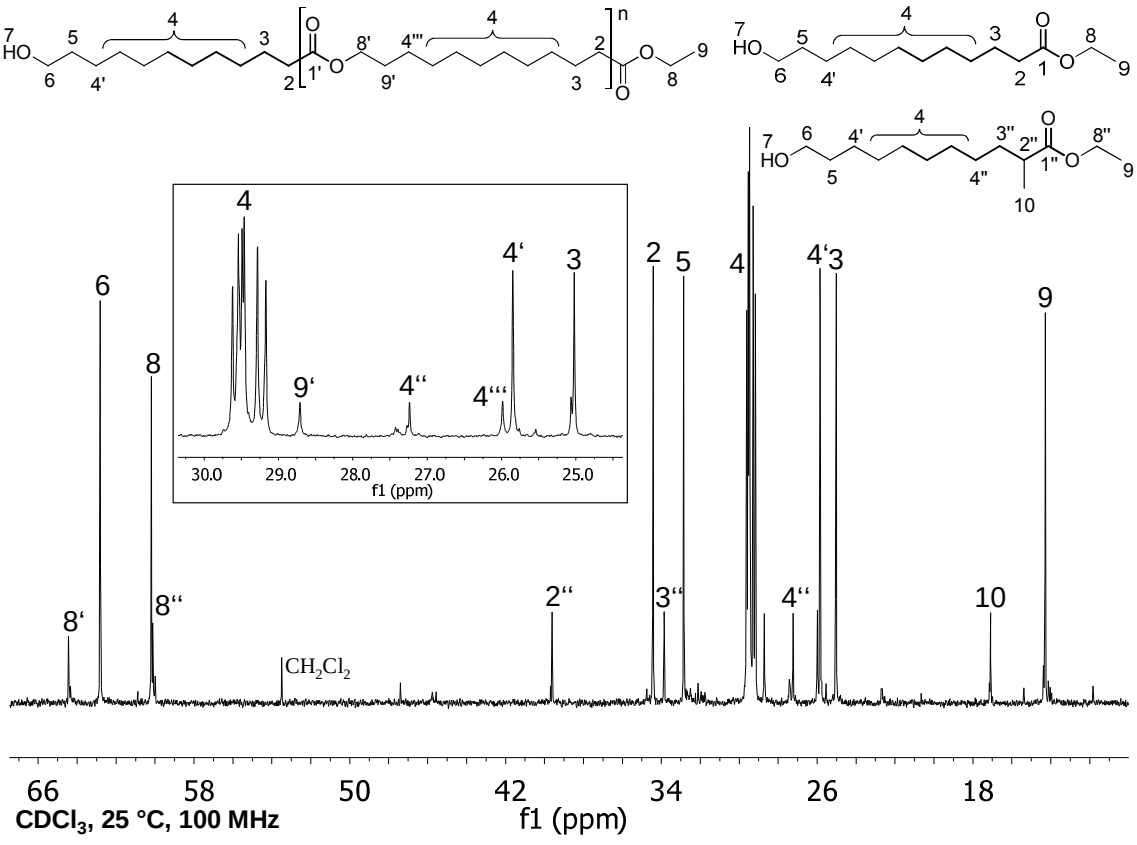


Figure A 12 Details of [13]C-NMR spectrum of ethyl-12-hydroxydodecanoate (Table 4.3, entry 4).

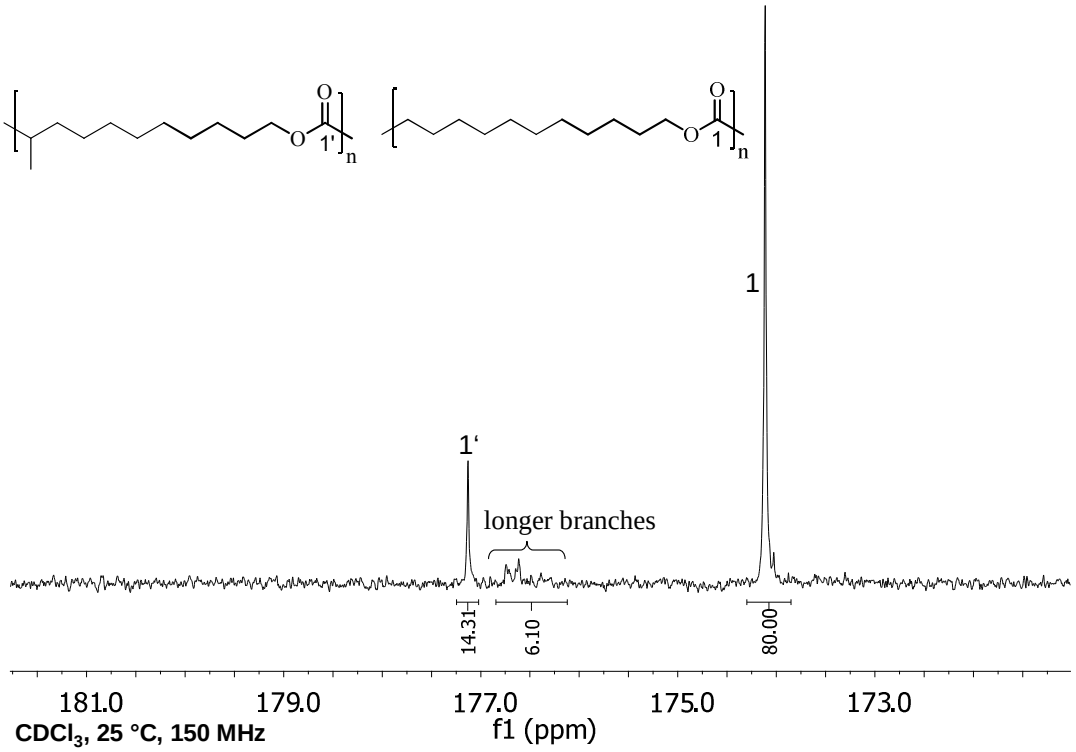


Figure A 13 Carbonyl region of ^{13}C-NMR spectrum of poly(dodecyloate) from ethyl-12-hydroxydodecanoate.

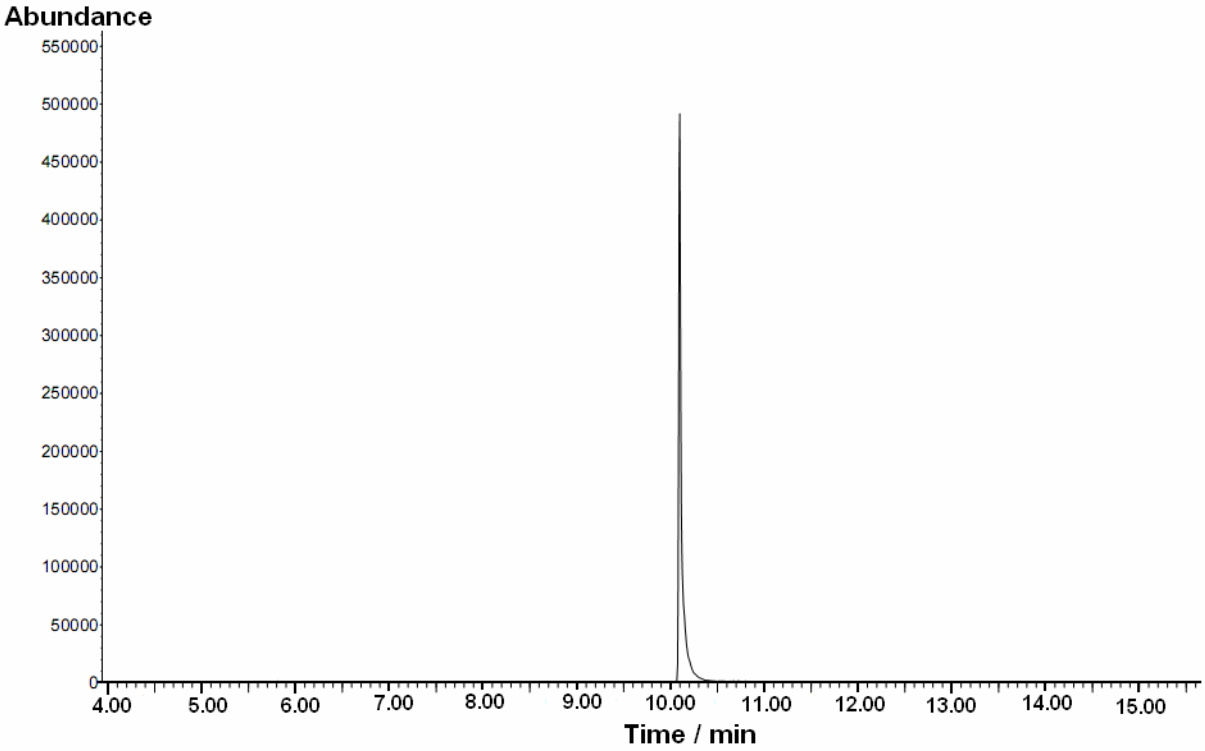


Figure A 14 Gas chromatogram of isolated dimethyl-1,19-nonadecanedioate (Table 5.1, entry 1).

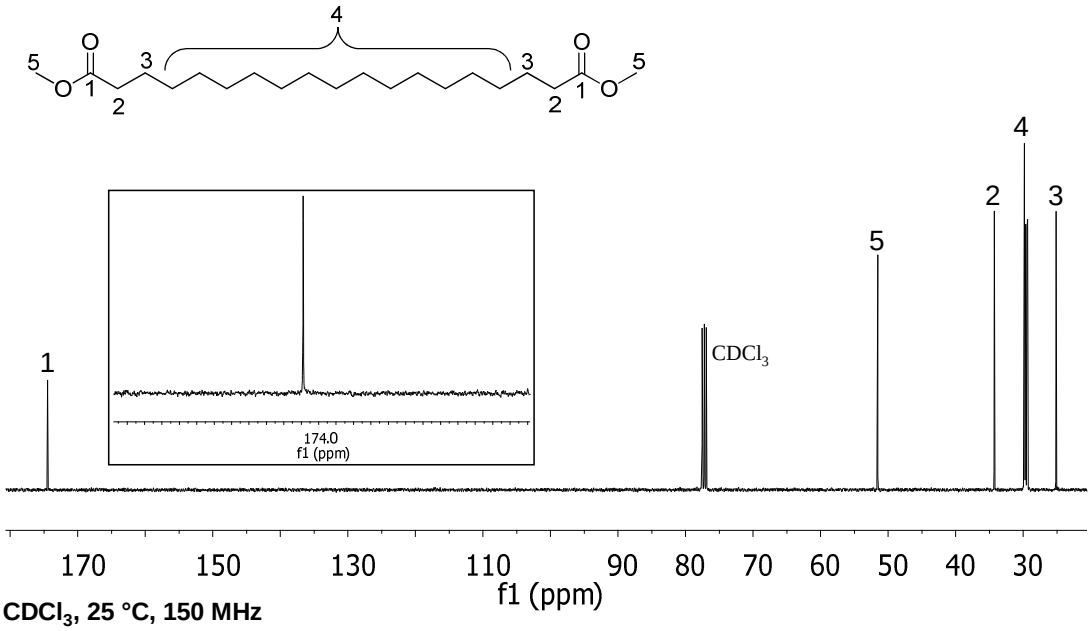


Figure A 15[13]C-NMR spectrum of isolated dimethyl-1,19-nonadecanedioate. Insert shows enlargement of the carbonyl region.[36]

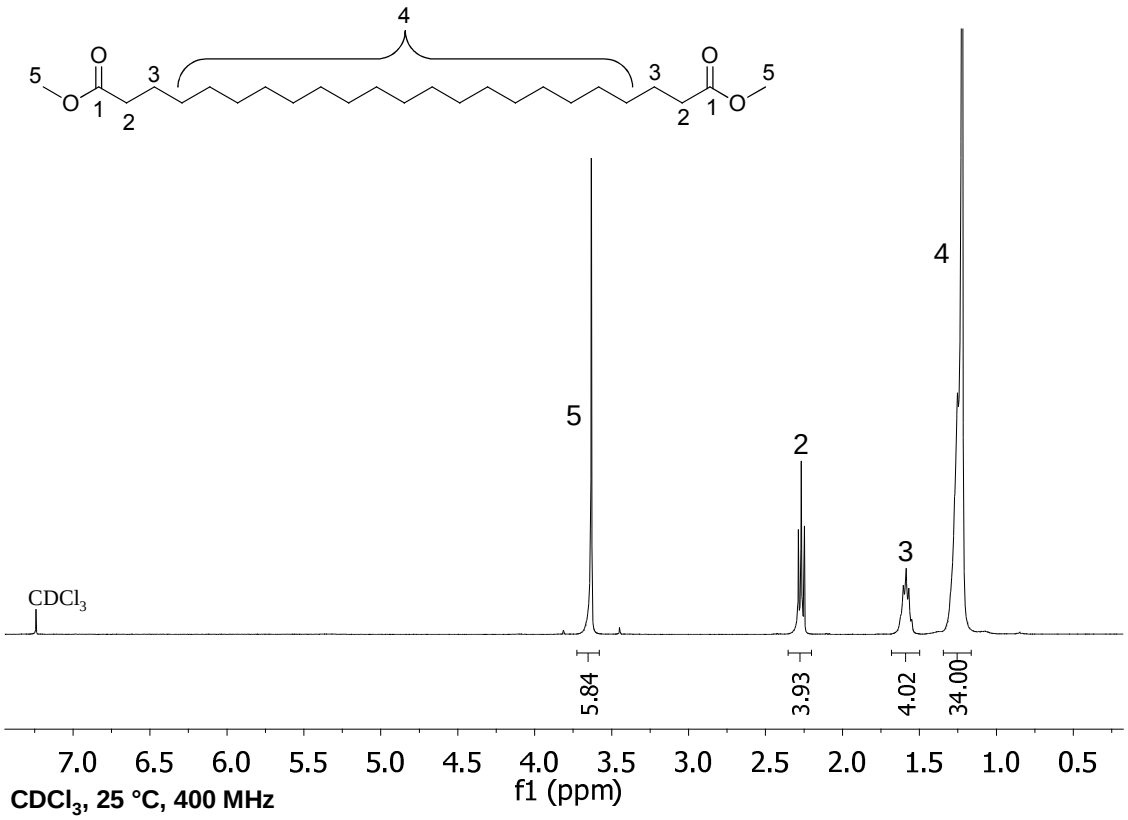


Figure A 16[1]H-NMR spectrum of dimethyl-1,23-tricosanedioate (Table 5.2, entry 3).

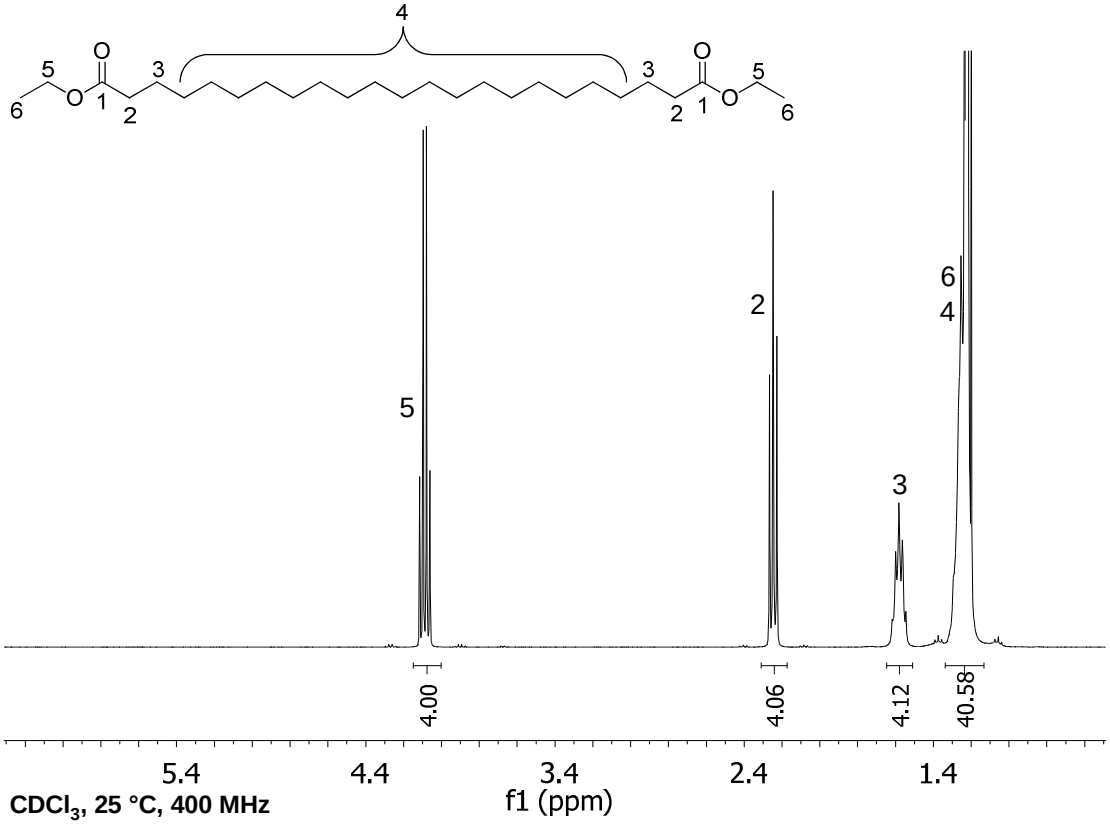


Figure A 17[1]H-NMR spectrum of diethyl-1,23-tricosanedioate (Table 5.2, entry 1).

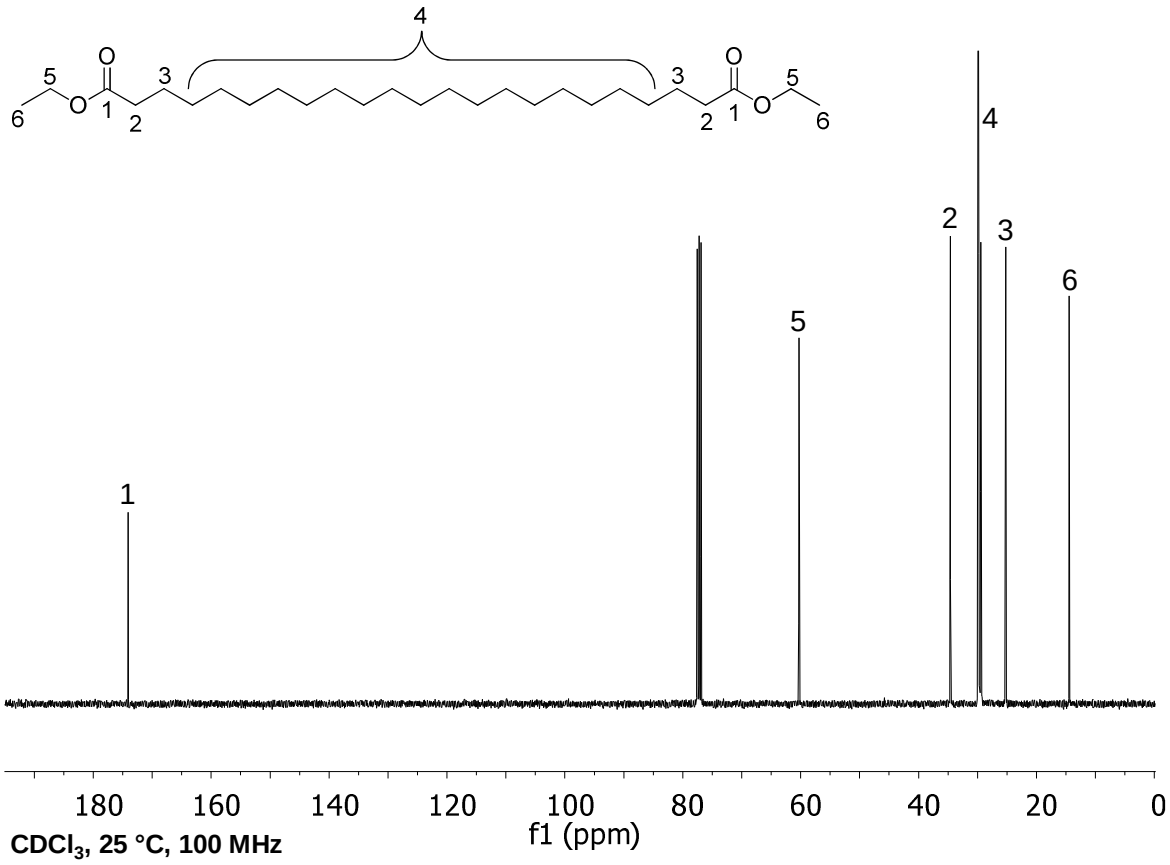


Figure A 18[13]C-NMR spectrum of diethyl-1,23-tricosanedioate (Table 5.2, entry 1).

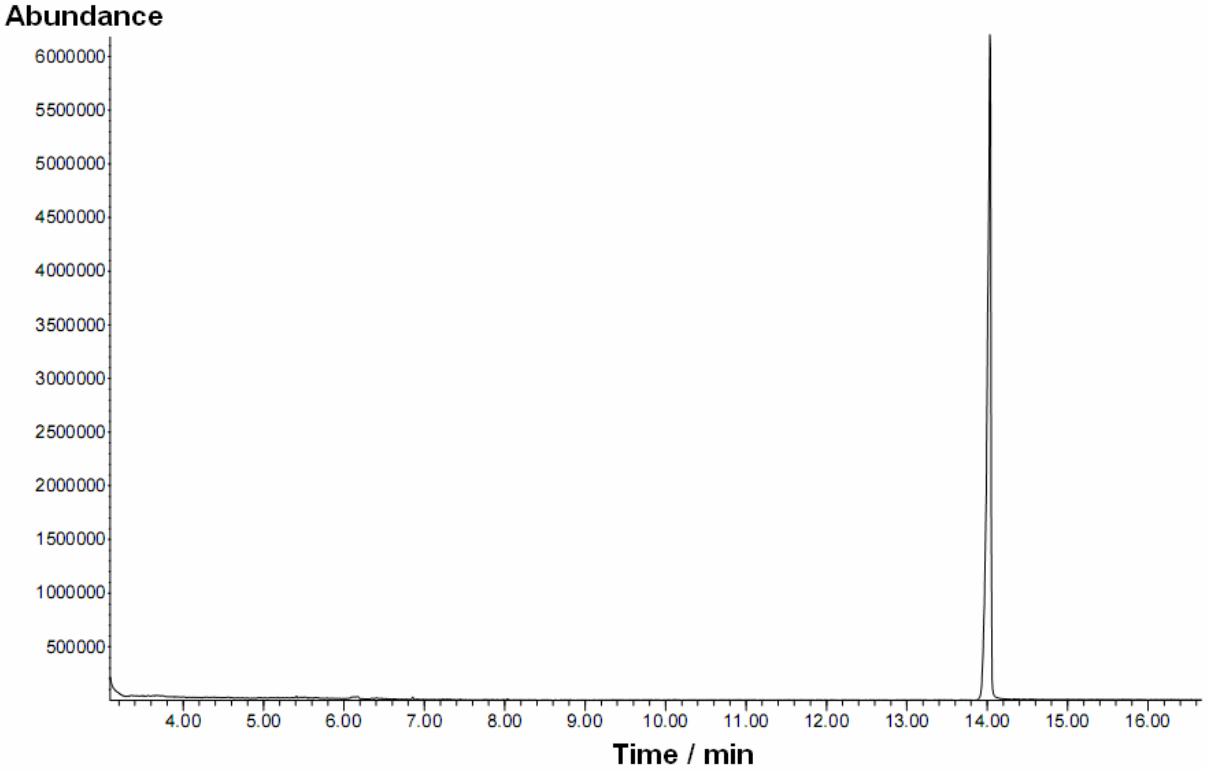


Figure A 19 Gas chromatogram of isolated diethyl-1,23-tricosanedioate (Table 5.2, entry 1).

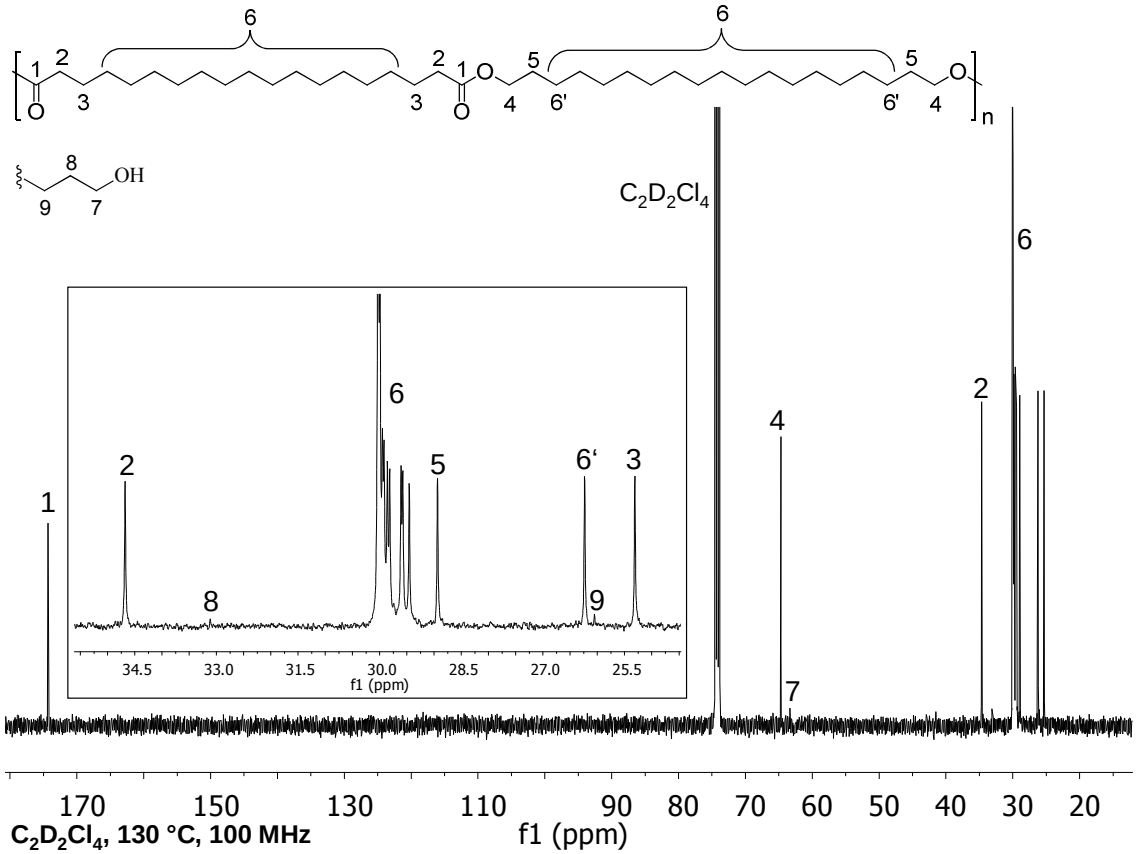


Figure A 20^{13}C-NMR spectrum of poly(1,19-nonadecadiyl-1,19-nonadecanedioate).

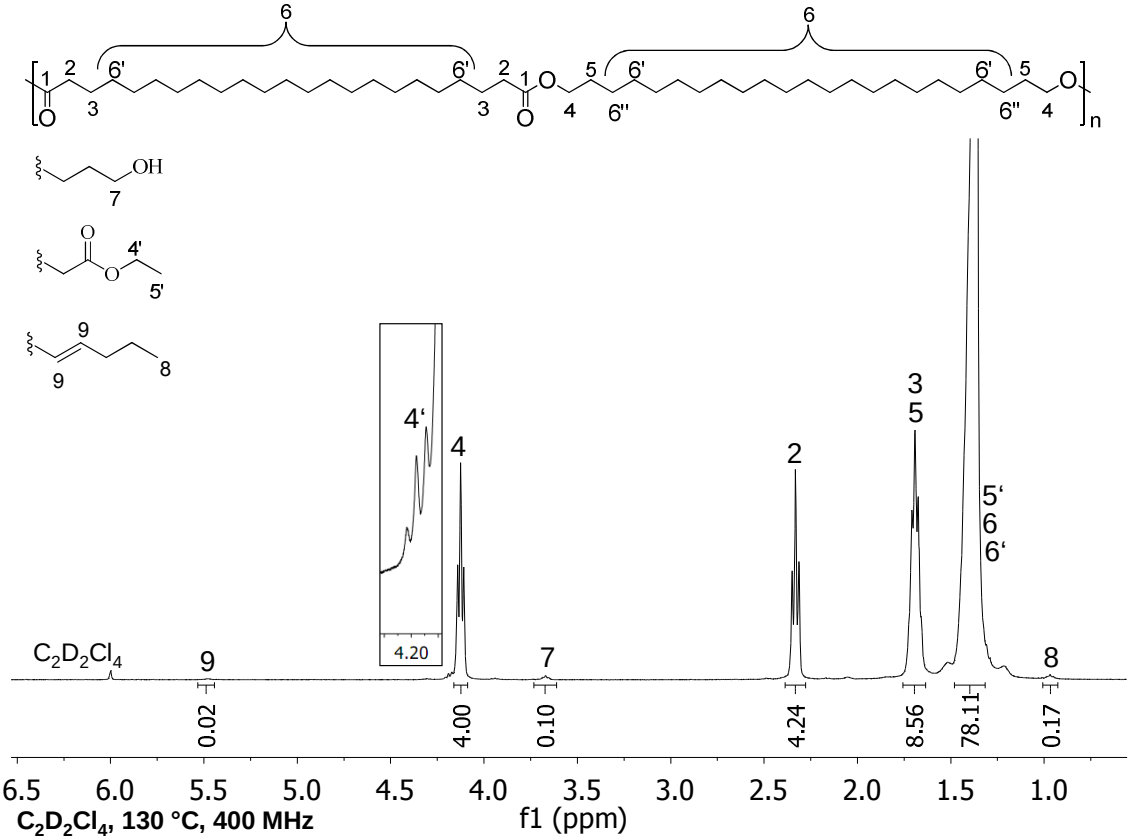


Figure A 21[1]H-NMR spectrum of poly(1,23-tricosadiyl-1,23-tricosanedioate).

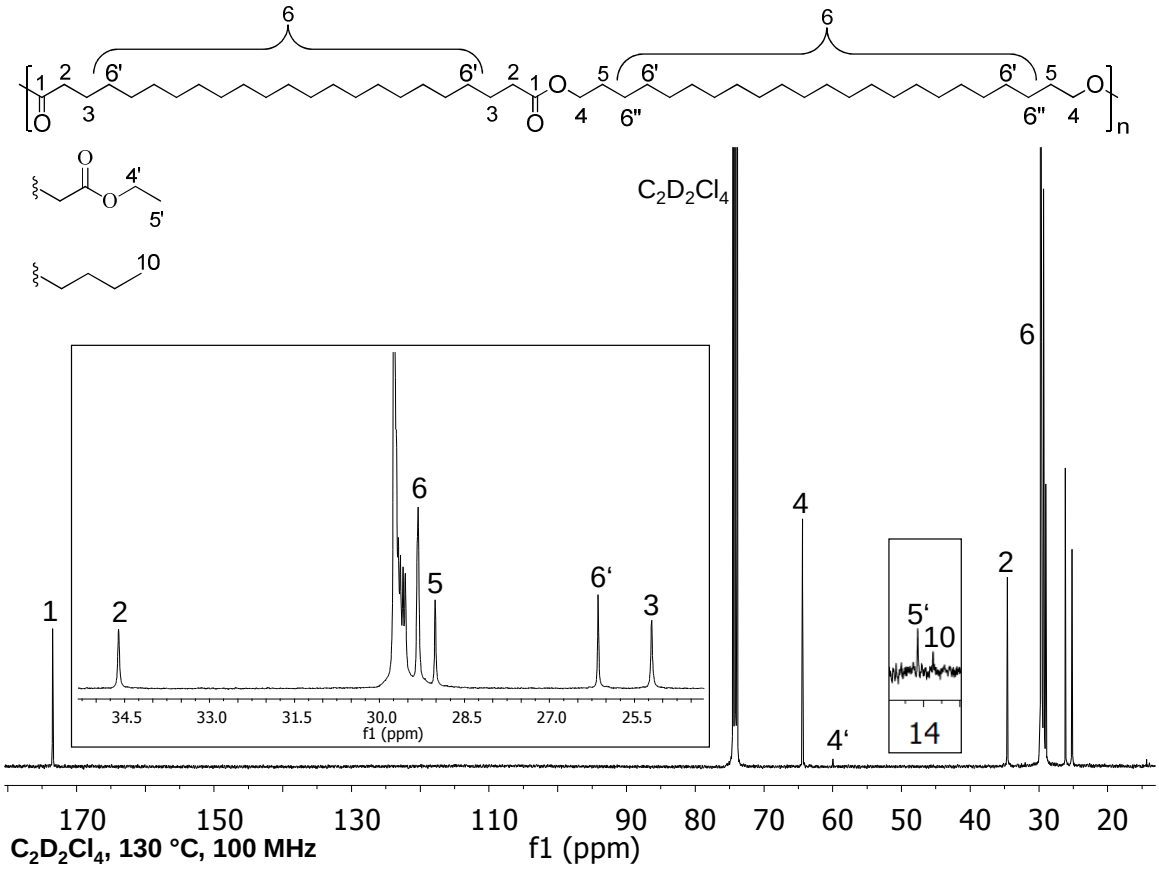


Figure A 22[13]C-NMR spectrum of poly(1,23-tricosadiyl-1,23-tricosanedioate).

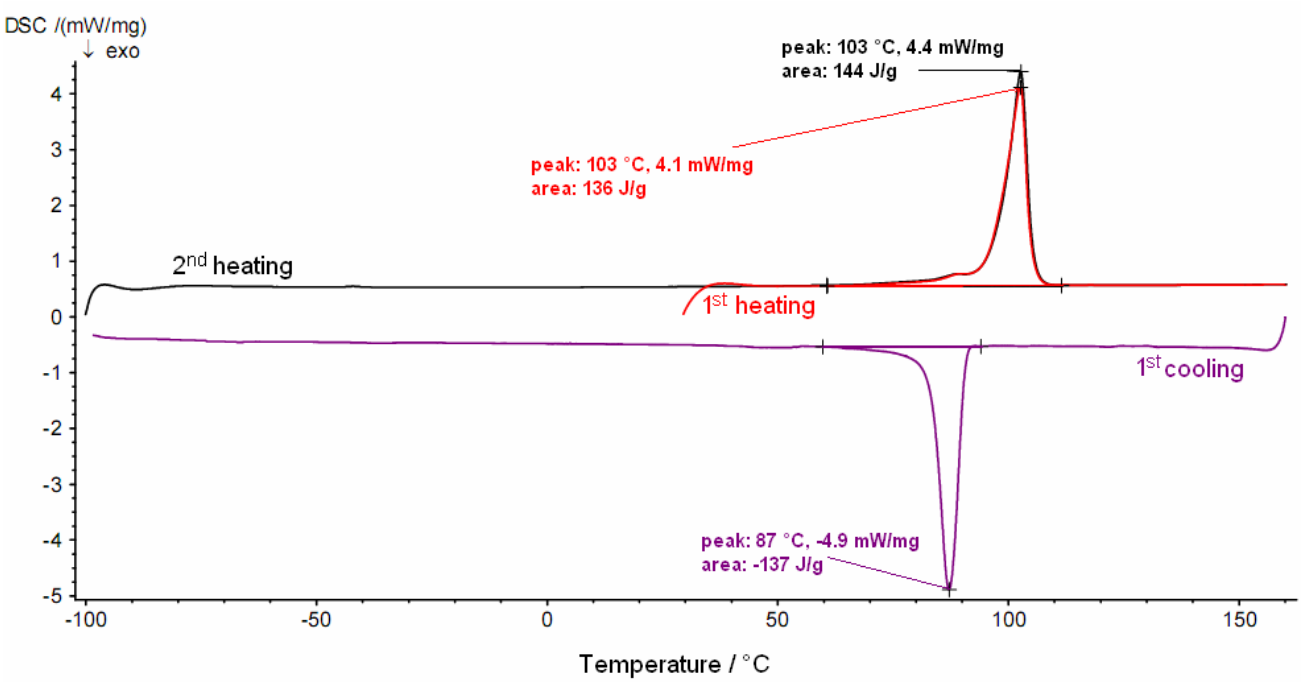


Figure A 23DSC trace of poly(1,19-nonadecadiyl-1,19-nonadecanedioate).

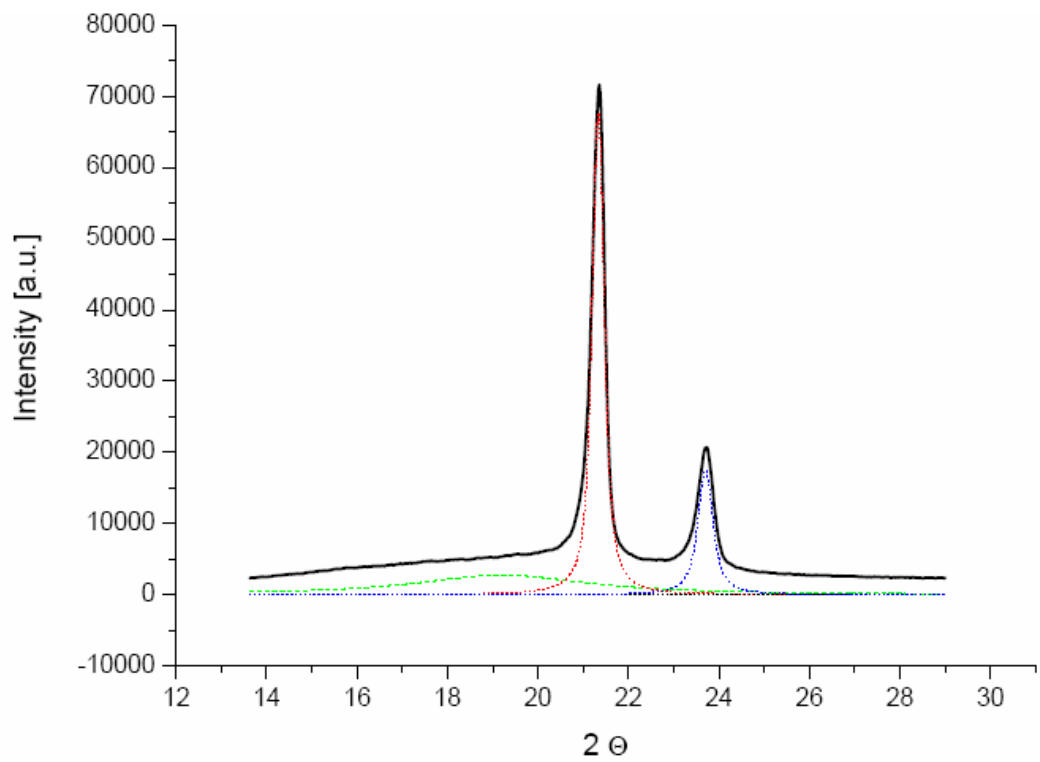


Figure A 24WAXS diffraction pattern of poly(1,23-tricosadiyl-1,23-tricosanedioate): enlargement of region 12 to 31° with contributions of amorphous halo (green) and 110 (red) and 200 (blue) reflection (bottom; deconvolution vertically displaced for clarity).

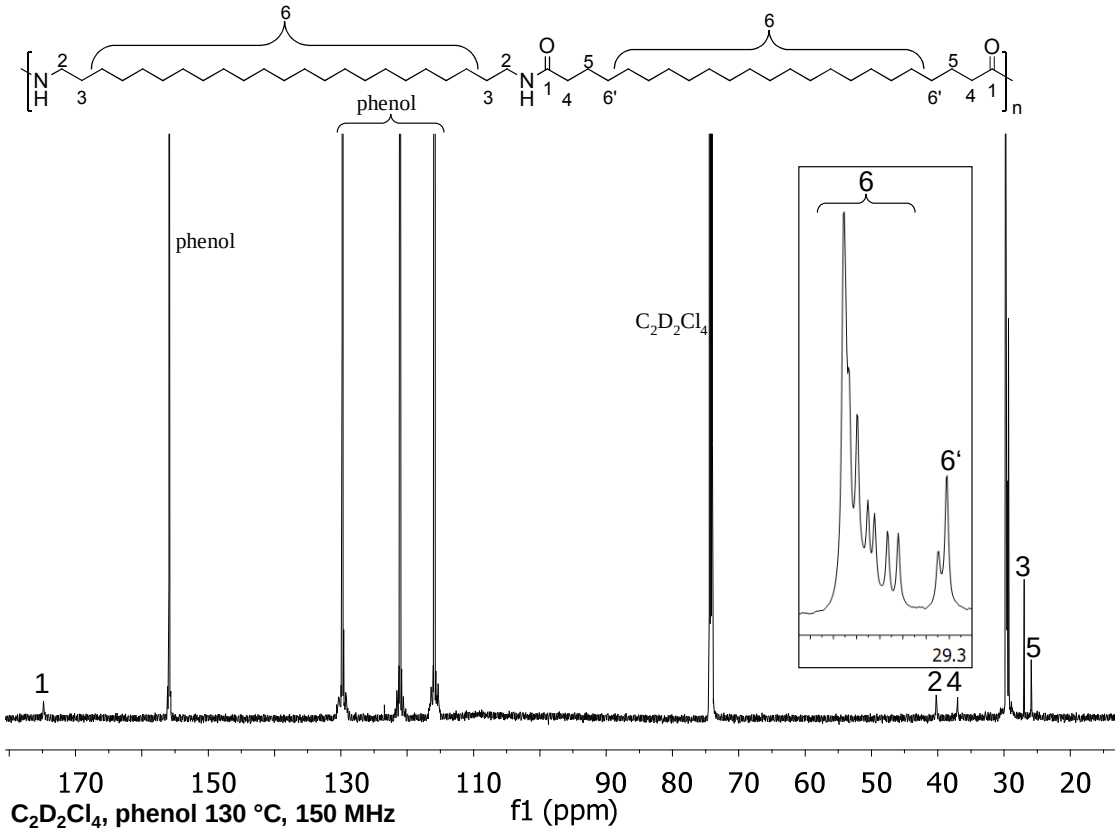


Figure A 25[13]C-NMR spectrum of PA 23 23.

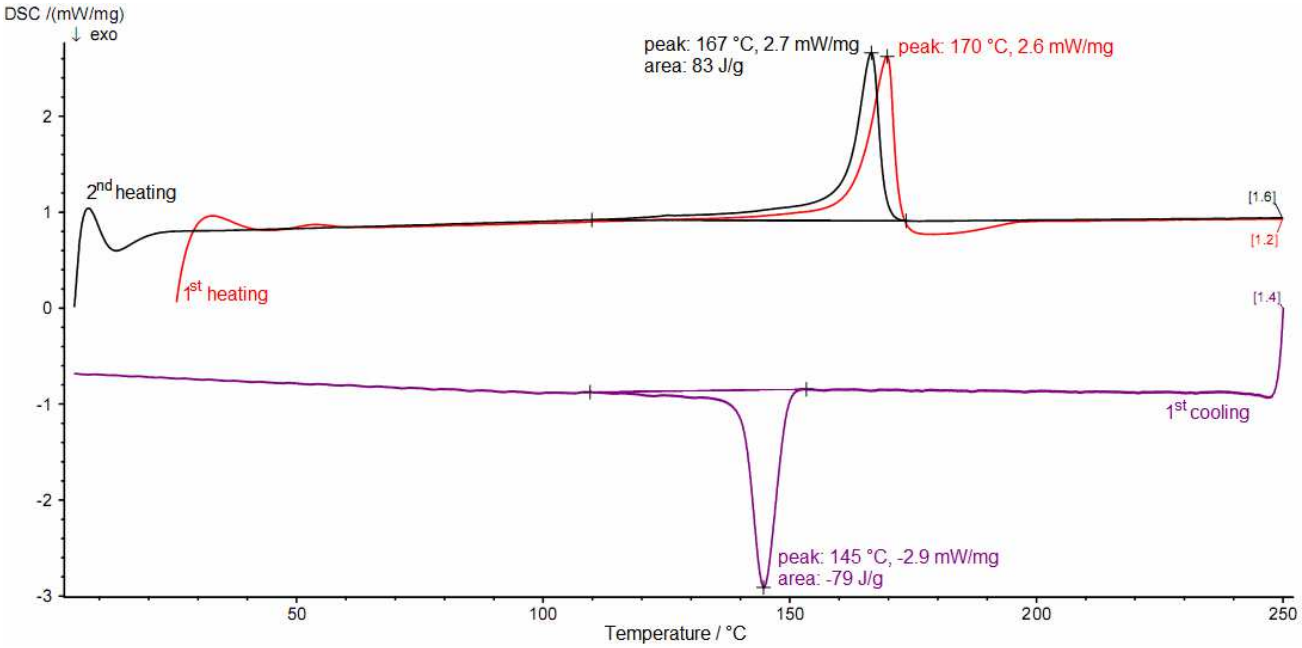


Figure A 26DSC trace of PA 11 19.

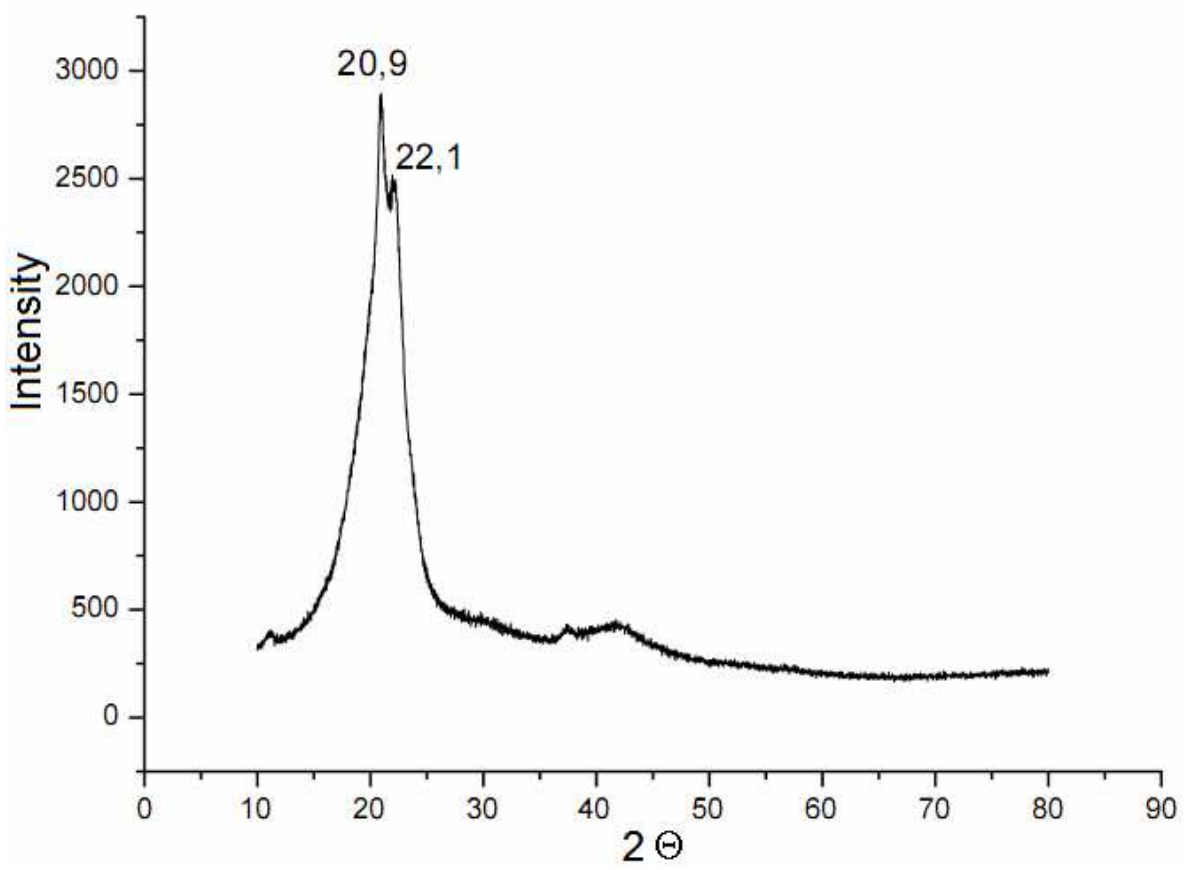


Figure A 27WAXS diffraction pattern of PA 11 19.

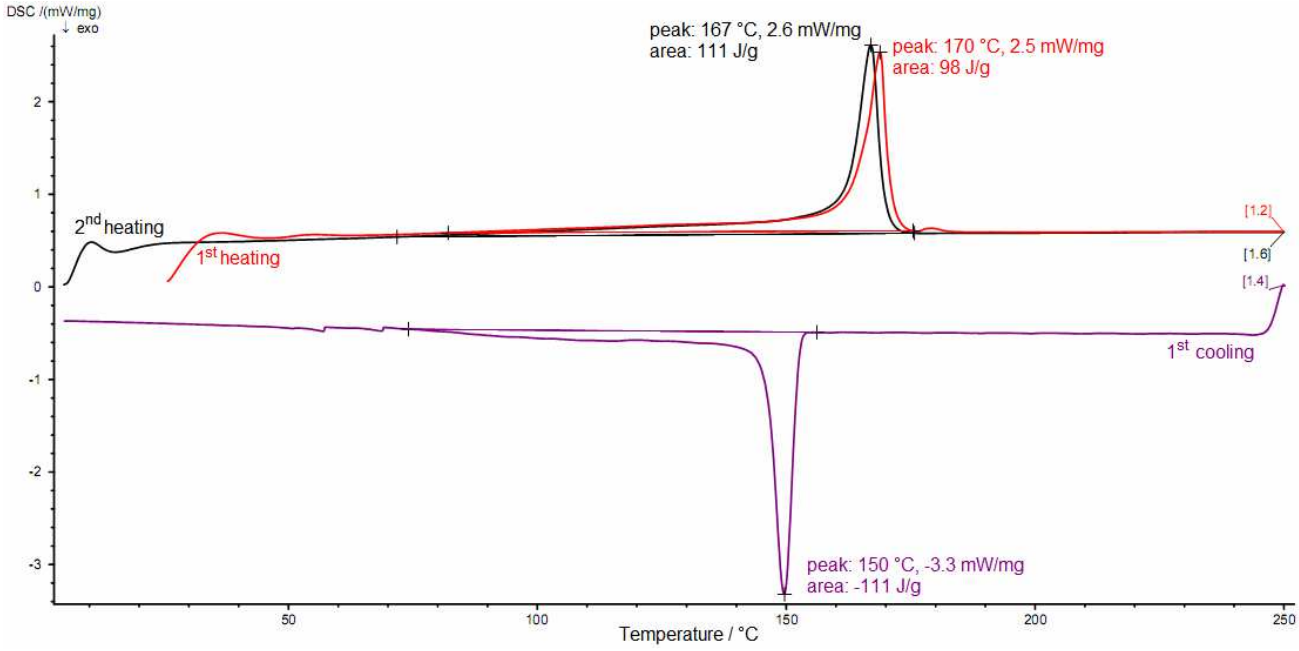


Figure A 28DSC trace of PA 11 23.

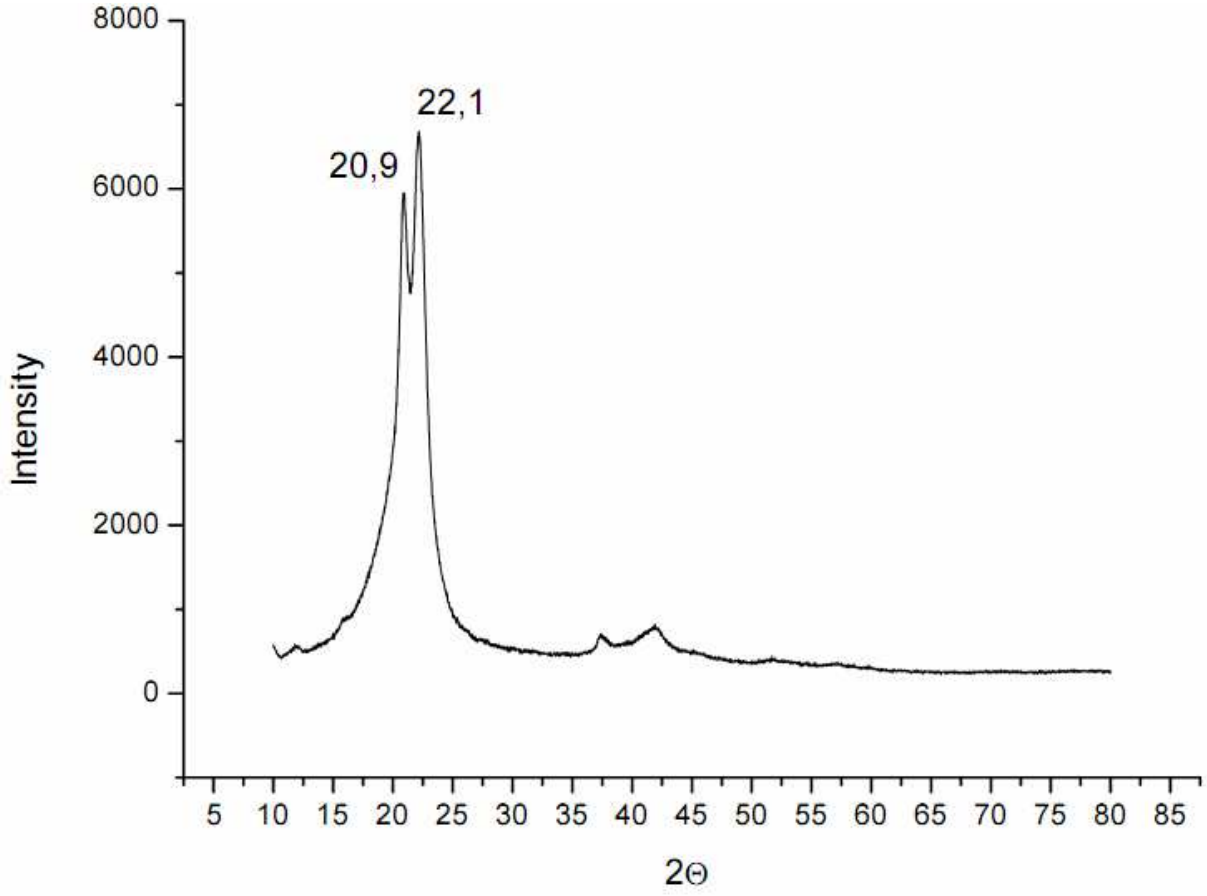


Figure A 29WAXS diffraction pattern of PA 11 23.

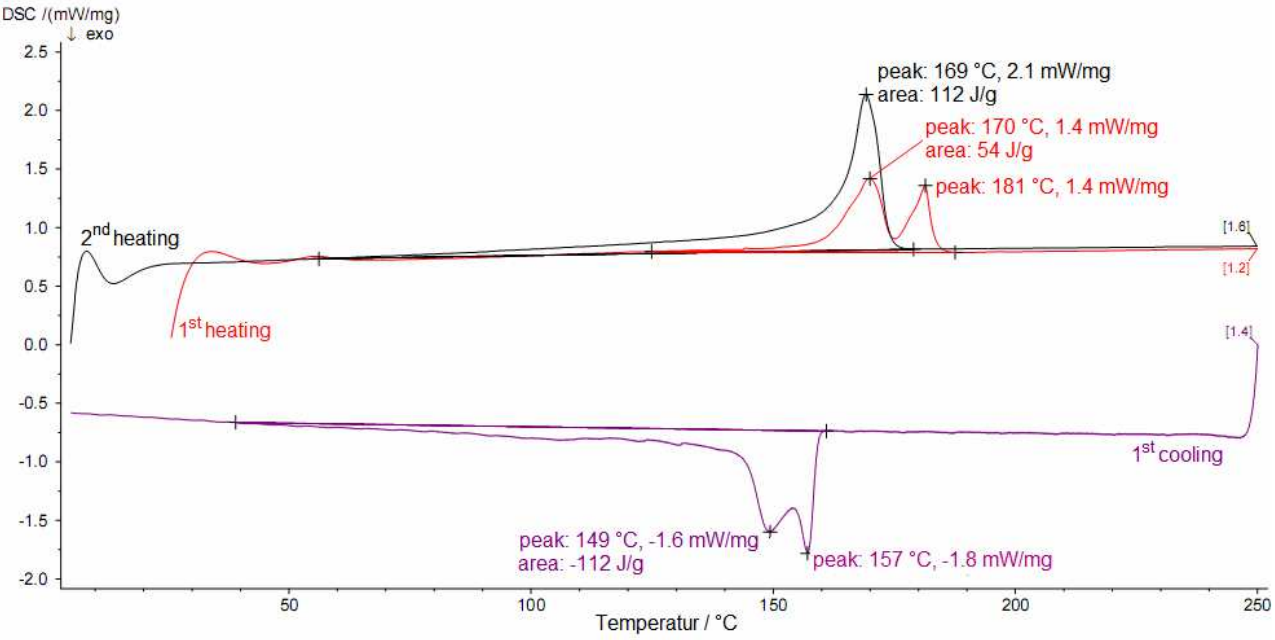


Figure A 30DSC trace of PA 12 19.

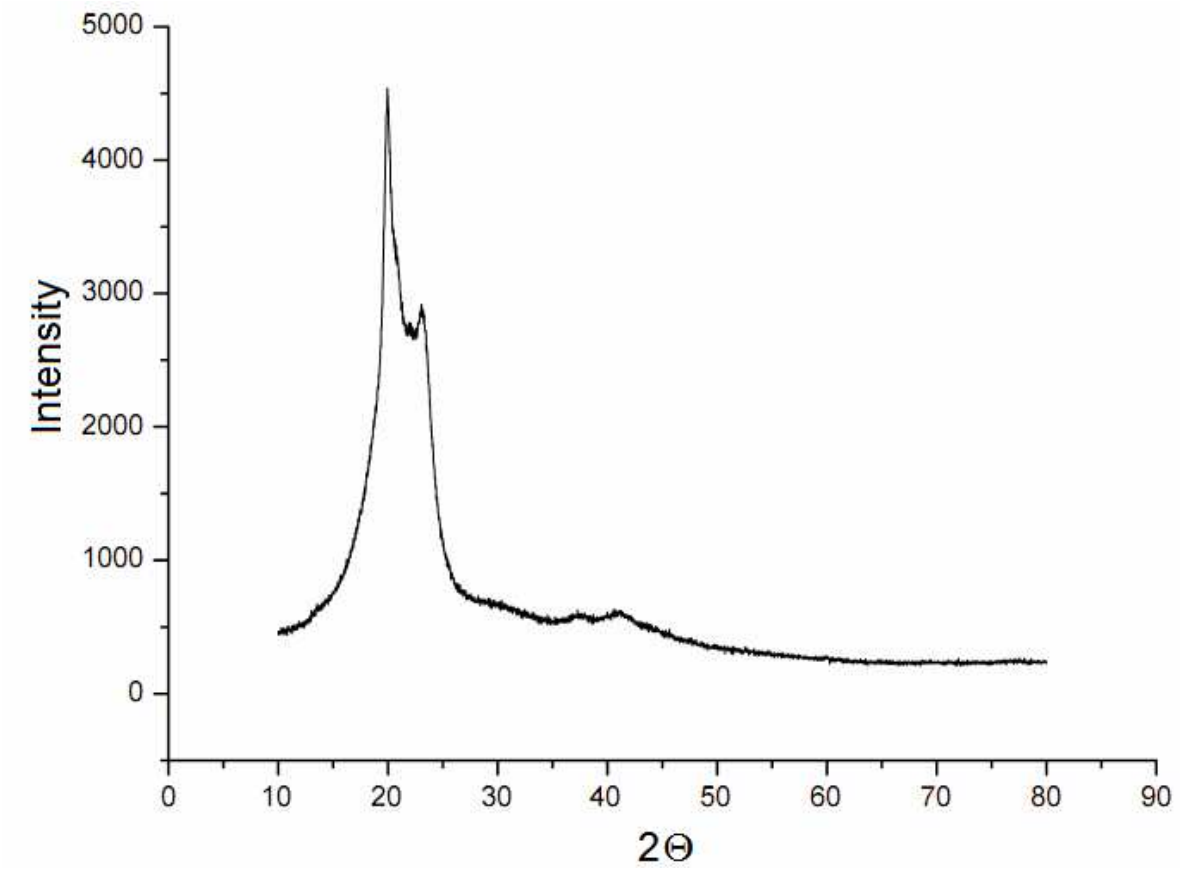


Figure A 31WAXS diffraction pattern of PA 12 19.

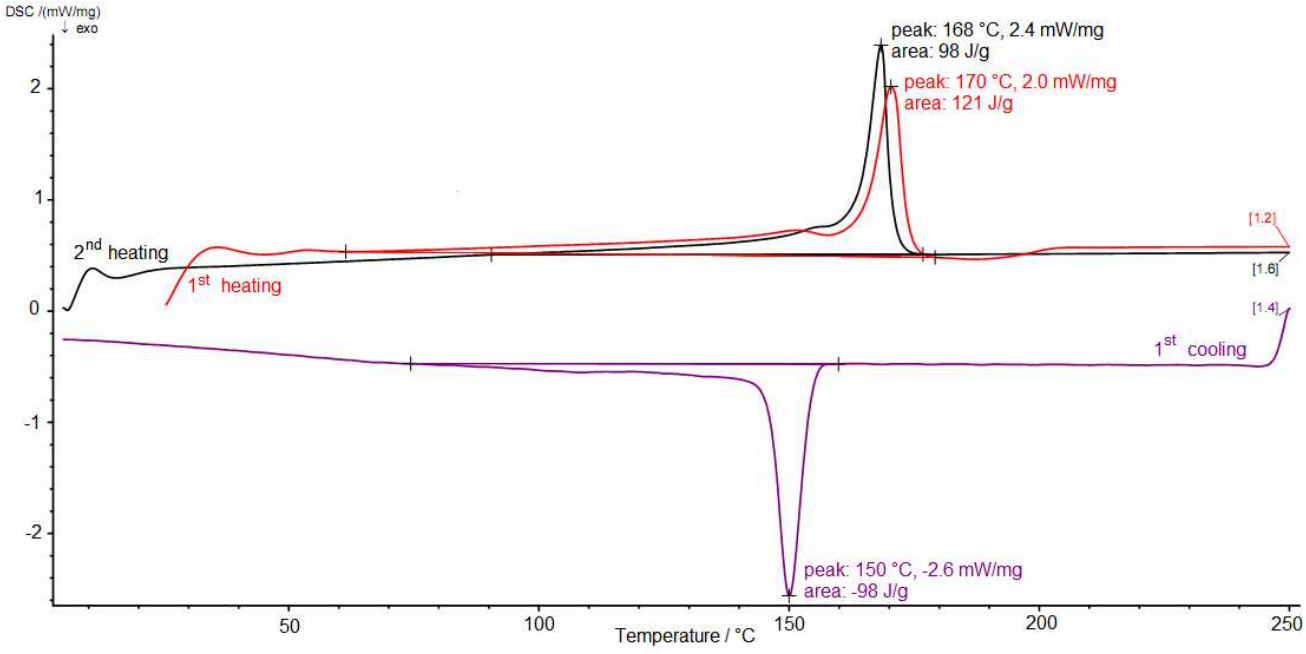


Figure A 32DSC trace of PA 12 23.

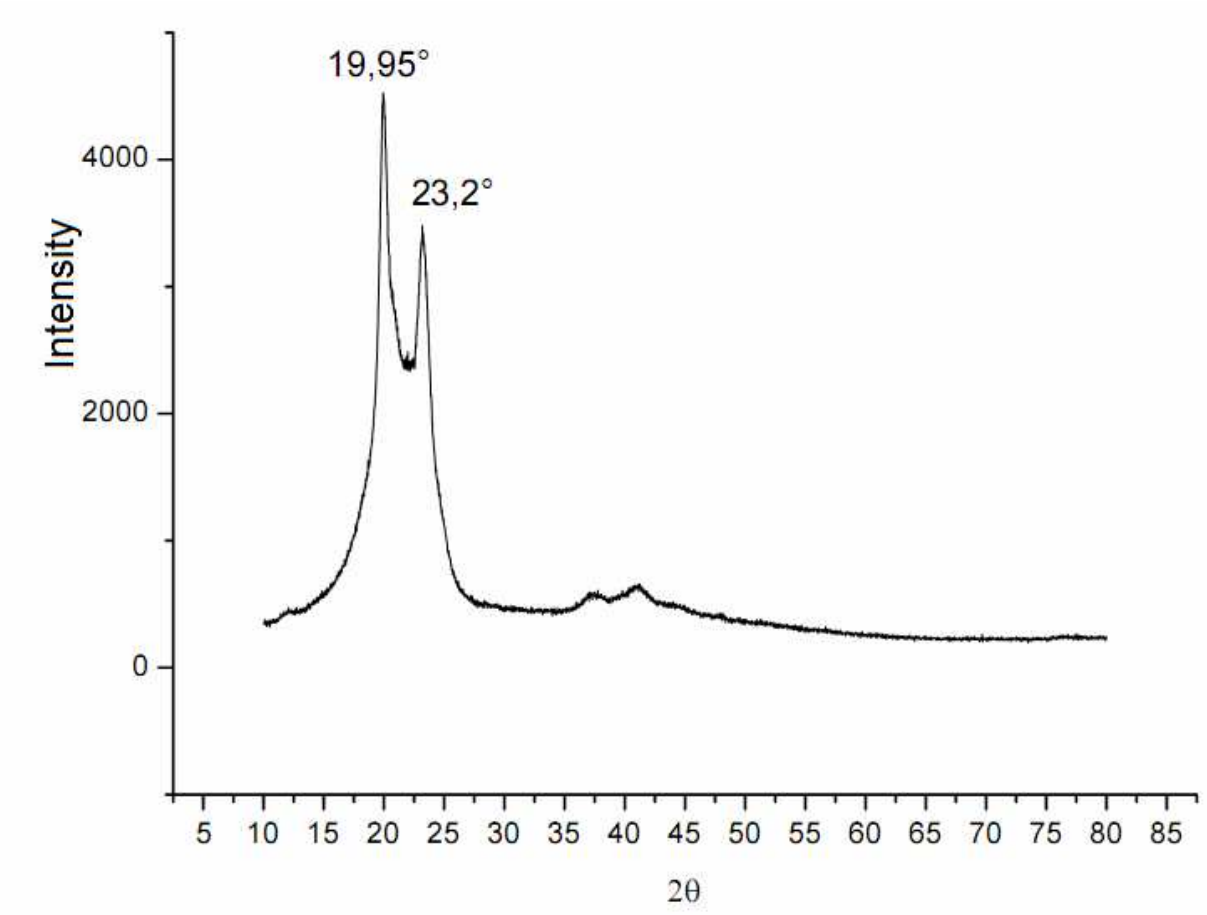


Figure A 33WAXS diffraction pattern of PA 12 23.

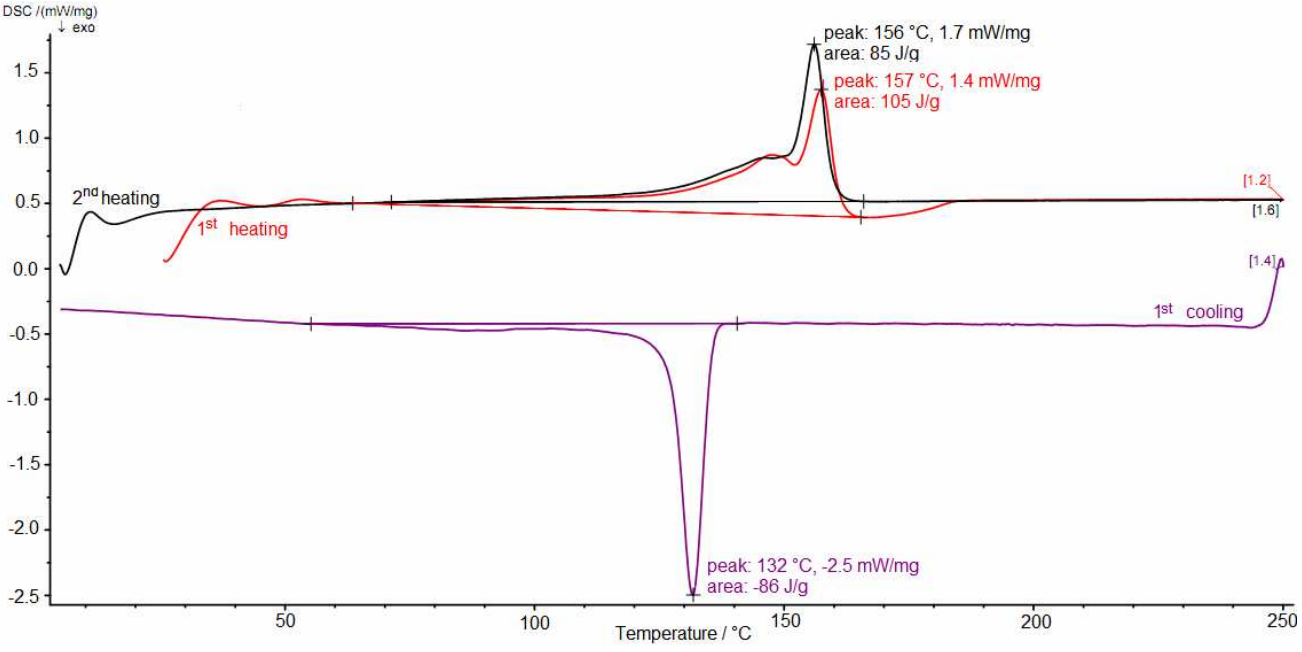


Figure A 34DSC trace of PA 23 19.

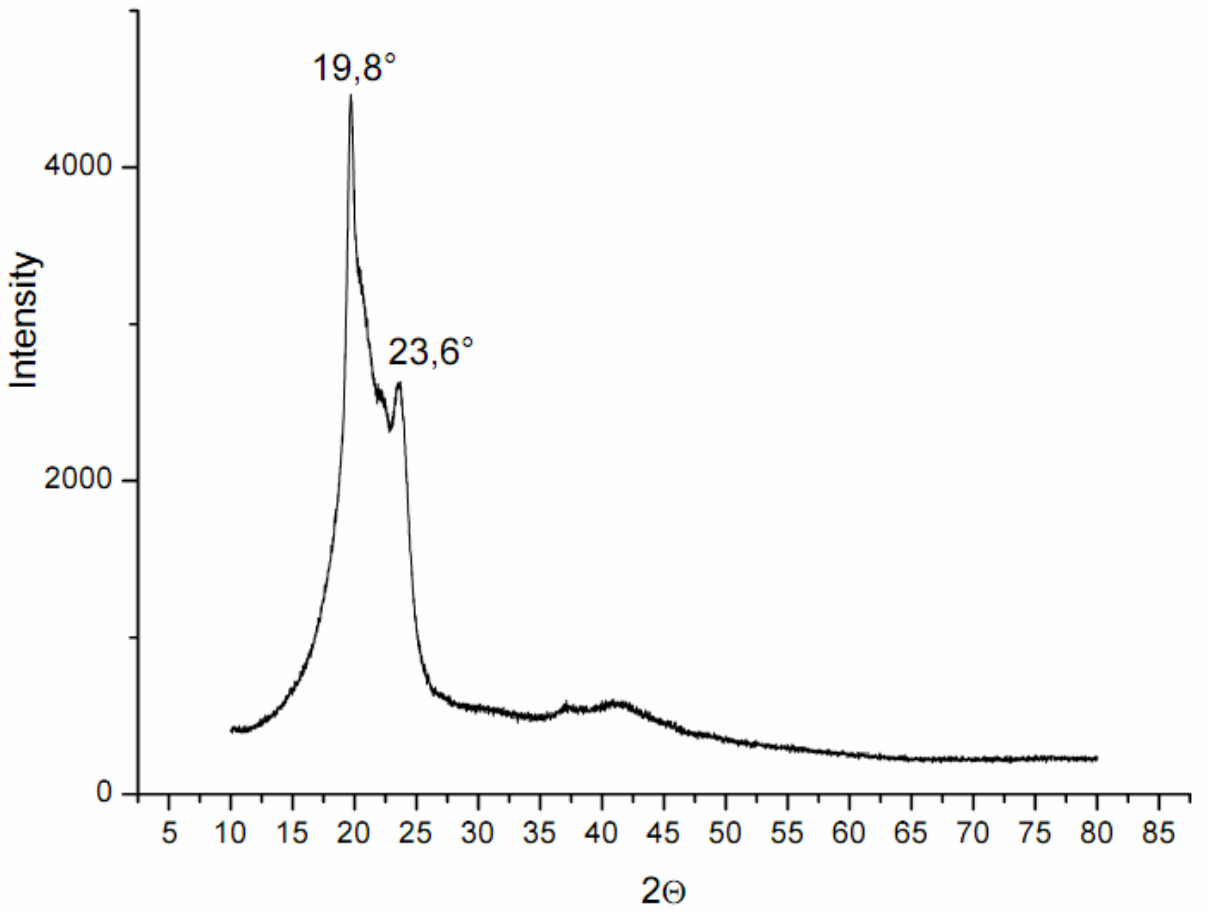


Figure A 35WAXS diffraction pattern of PA 23 19.

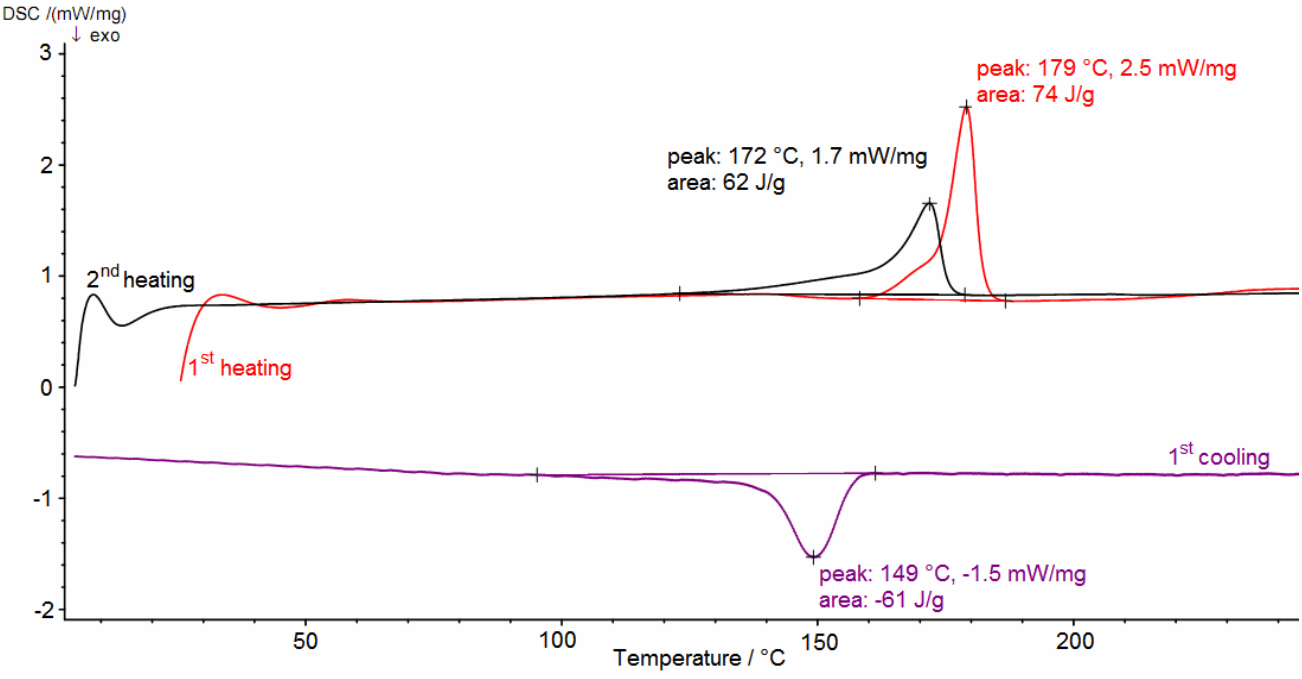


Figure A 36DSC trace of PA 12 12, synthesised by ruthenium catalysis.

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