

# Chain Multiplication of Fatty Acids to Precise Telechelic Polyethylene

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**Abstract:** Starting from common monounsaturated fatty acids, a strategy is revealed that provides ultra long aliphatic  $\alpha,\omega$  difunctional building blocks by a sequence of two scalable catalytic steps that virtually double the chain length of the starting materials. The central double bond of the  $\alpha,\omega$  dicarboxylic fatty acid self metathesis products is shifted selectively to the statistically much disfavored  $\alpha,\beta$  position in a catalytic dynamic isomerizing crystallization approach. "Chain doubling" by a subsequent catalytic olefin metathesis step, which overcomes the low reactivity of this substrates by using waste internal olefins as recyclable co reagents, yields ultra long chain  $\alpha,\omega$  difunctional building blocks of a precise chain length, as demonstrated up to a  $C_{48}$  chain. The unique nature of these structures is reflected by unrivaled melting points ( $T_m=120^\circ\text{C}$ ) of aliphatic polyesters generated from these telechelic monomers, and by their self assembly to polyethylene like single crystals.

Owing to their particular molecular structure, naturally occurring fatty acids are a feedstock of choice for the generation of molecules comprising long methylene sequences with an attached functional group. The generation of sebacic acid from castor oil is a well established example. This mid chain dicarboxylic acid is used as a monomer building block for high performance nylons<sup>[1]</sup> or biodegradable polyesters.<sup>[2]</sup> Recently developed catalytic routes allow for the preparation of other long chain  $\alpha,\omega$  difunctional compounds from readily available fatty acids, such that the product comprises the full length of a fatty acid chain. For example, dicarboxylic acids  $\text{HOOC}(\text{CH}_2)_n\text{COOH}$  with  $n=18$  or  $19$  can be generated from the  $C_{18}$  fatty acids oleic or stearic acid.<sup>[3,4]</sup>

Beyond these chain lengths, ultra long chain compounds with methylene sequences that significantly exceed the length of a typical fatty acid chain appear relevant from different perspectives. For instance, such structural motifs occur as ceramide,<sup>[5,6]</sup> a main component of the *stratum corneum* of the epidermis layer of the human skin, and they are part of the cellular walls of several algae species (algaenans)<sup>[7-11]</sup> and of plants (cutin and suberin).<sup>[12-14]</sup> The highly hydrophobic nature of the  $\alpha,\omega$  difunctional building blocks here is exploited to generate an insoluble polymer, protecting the

organisms from undesired influences from their environment as well as from water loss. From a different viewpoint, their length corresponds to the typical thickness of phospholipid bilayers, which offers possibilities for synthetic structures mimicking these ubiquitous structures of biological systems.<sup>[15]</sup> Further, such chain lengths are also found as the typical thickness of crystalline lamellae in polymers, which determines their materials properties. This suggests that there are specific lengths of a methylene sequence, which show an extraordinary strong driving force for crystallization. Artificial ultra long chain compounds with these lengths thus might be powerful building blocks for various crystalline materials.

However, the very limited perspectives for accessing such compounds efficiently has discouraged broader studies of their properties and potential. Reported strategies for the synthesis of aliphatic  $\alpha,\omega$  difunctional building blocks with a chain length greater than  $C_{30}$  commonly comprise tedious multi step reaction sequences. For example, multiple cycles of Wurtz coupling of  $\alpha$  halo  $\omega$  alcohols can be used for the preparation of a  $C_{44}$  diol.<sup>[16]</sup> Catalytic methods have also been investigated, as reported by Augustin and Schäfer in a Glaser coupling starting from oleic acid.<sup>[17]</sup> Yet again, laborious steps for the preparation of a terminal acetylene are required to access the desired bis(triunsaturated)  $C_{36}$   $\alpha,\omega$  diester. Additionally, the reagents and by products involved in all these procedures are prohibitive to performing them on larger scales. As an example of entirely different polymerization approaches, catalyzed chain growth of ethylene can yield difunctional chains. Limitations of these approaches are imprecise chain lengths and imperfect end group fidelity. Additionally, in most cases specific functionalized magnesium reagents and additional post polymerization steps are required that are not well suited for large scales.<sup>[18-20]</sup>

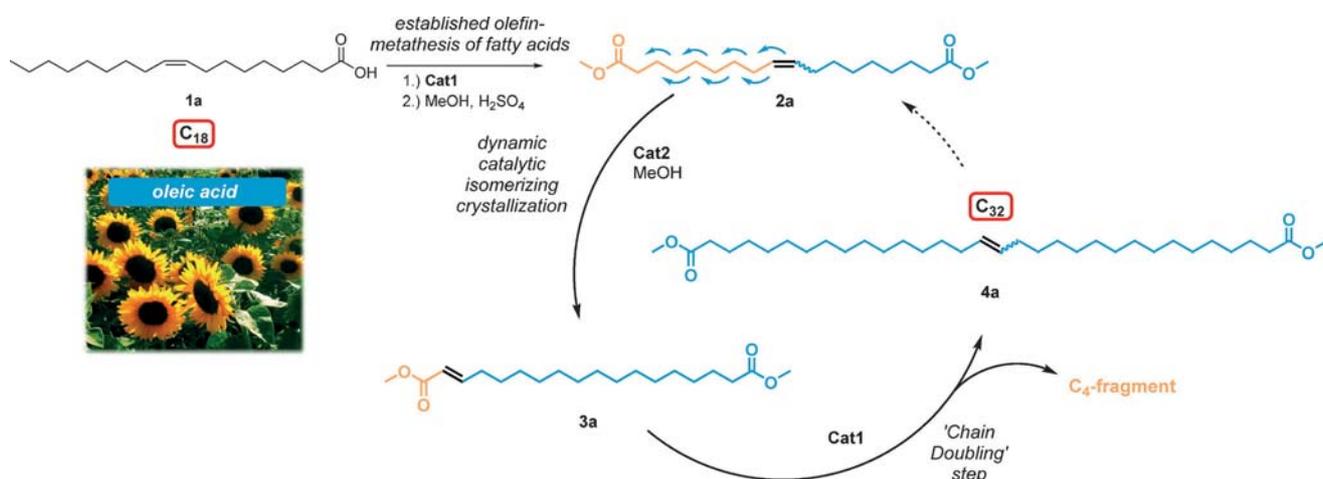
We now report an approach that allows for the doubling of the chain length of readily available fatty acid starting materials, employing catalyzed steps exclusively which also do not consume further reagents and do not generate excessive amounts of undesired side products. With this technique,  $\alpha,\omega$  difunctional building blocks with a  $C_{48}$  chain can be accessed that open opportunities as exemplified by self assembled structures and crystalline materials.

Self metathesis of unsaturated fatty acid derivatives, as a well established and industrially used process,<sup>[21]</sup> allows the synthesis of internally unsaturated dicarboxylic compounds. These reactions, generally leading to equilibrium mixtures of products and starting material, can be driven in a favorable direction by choosing appropriate reaction conditions.<sup>[22,23]</sup>

By application of Hoveyda Grubbs second generation complex (**Cat1**) as a metathesis catalyst, the reaction equilibrium of oleic acid (**1a**) can be driven to the diacid (and stoichiometric amounts of octadecene) by its precipitation from the reaction mixture.

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**Scheme 1.** The “chain doubling” strategy for the preparation of ultra long chain  $\alpha,\omega$  diester **4a**.

Our concept for chain multiplication relies on a selective shift of the double bond toward a chain end, starting from the above self metathesis product. From here, an olefin metathesis step will result in a virtual doubling of the chain length, with expulsion of only a small  $C_4$  fragment (Scheme 1). The internal double bond of the chain doubled products offers itself for hydrogenation for example to generate ultra long chain  $\alpha,\omega$  difunctional saturated compounds.

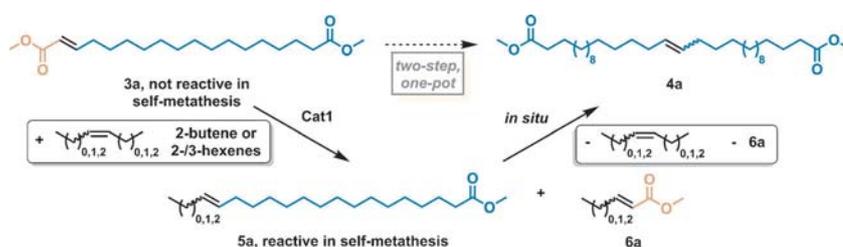
To promote isomerization of the internal double bond of the starting material, we employed  $[(dtbpx)Pd(OTf)_2]$  (**Cat2**), bearing the electron rich, bulky diphosphine 1,2 bis{(di *tert* butylphosphino)methyl}benzene (dtbpx) ligand, as a highly active catalyst.<sup>[24–26]</sup> Upon exposure of diester **2a** to a methanolic solution of 0.5 mol % of **Cat2**, an equilibrium of the isomers of the unsaturated diester differing in the position of the double bond along the chain is attained rapidly. The slightly higher stability of the target  $\alpha,\beta$  unsaturated ester **3a** reflects in a slight preference for **3a** in an otherwise statistical isomerization equilibrium. That is, at 30 °C the  $\alpha,\beta$  unsaturated isomer **3a** is present in 11.7% with a (*E/Z*) ratio of 55 (Supporting Information, Figure S1).

To achieve a full conversion into **3a**, a physical separation from the continuously catalyzed dynamic equilibrium was employed. From screening of a range of solvents, and temperature sequences, a crystallization from methanol evolved as condition of choice. Owing to its slightly different polarity and lower solubility, crystallization of **3a** occurs preferentially despite its comparatively low concentration in the equilibrium of the double bond isomers. In combination with continuous replenishment by the ongoing isomerization equilibrium, this provides a net driving force for conversion of **2a** into **3a**. In this batch type procedure, a decreasing concentration of the double bond isomers in their entirety in solution with increasing amount of already crystallized material is compensated by decreasing the temperature to maintain supersaturation. In this fashion, a virtually complete yield of

crystallized material (95%) could be obtained for diester **3a**. The selectivity for the desired  $\alpha,\beta$  unsaturated diester was 84%, as determined by  $^1H$  NMR spectroscopy. That is, by the dynamic catalytic isomerizing crystallization procedure the thermodynamic isomer composition can be overcome in favor of the desired  $\alpha,\beta$  unsaturated isomer. From the crude products, pure ( $\geq 99\%$ ) **3a** was obtained by recrystallization in 70% overall yield. The remaining internal isomer material can be recycled to the dynamic isomerization/crystallization.<sup>[27]</sup>

With this material in hand, we pursued a “chain doubling” method to the desired ultra long chain structures through olefin metathesis. A direct self metathesis of the  $\alpha,\beta$  unsaturated diesters did not proceed with satisfactory yields, and **4a** was only formed to a minor extent.<sup>[28]</sup> Apparently, the electron deficient character of the olefinic bond in **3a** reduces its reactivity to such an extent that no significant self metathesis occurs.<sup>[29]</sup> To overcome this problem, intermittent alkenolysis with electron richer and more reactive short chain olefins was performed (Scheme 2). Readily available, low cost 2-butene or a mixture of internal hexene isomers, respectively, were employed (for further information on alkenolysis of **3a**, see the Supporting Information).

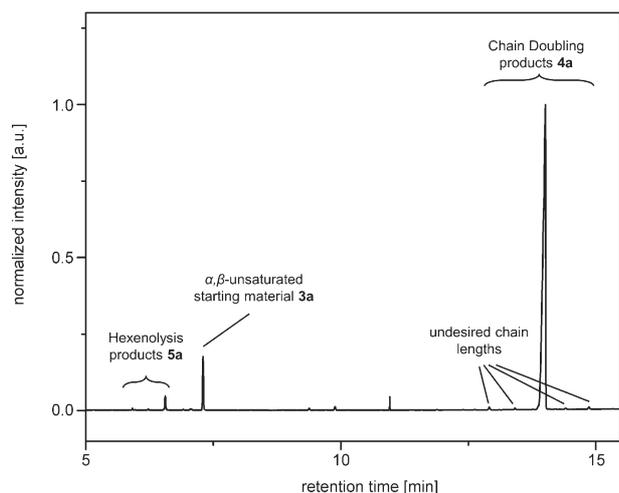
To favor a high conversion of **3a**, the short chain olefin co reagent was used in excess. In a two step, one pot approach, first the cross metathesis was performed with **Cat1**, followed by an in situ self metathesis step of the generated monoesters **5a**. The latter self metathesis could be induced by simply



**Scheme 2.** “Chain doubling” of  $\alpha,\beta$  unsaturated diester **3a** via cross metathesis with short chain olefins.

applying vacuum to the reaction vessel. By this procedure, more than 95 % of the starting material could be transformed into the desired ultra long chain diester **4a**.

A potential pitfall in this concept is double bond isomerization at this stage, a ubiquitous reaction in the presence of ruthenium metathesis catalysts.<sup>[30–32]</sup> This would lead to products of variable chain lengths. To this end, isomerization could be suppressed virtually completely by the choice of appropriate reaction conditions, particularly reaction times and the presence of 1,4 benzoquinone. Hereby, selectivities for the target chain lengths of  $\geq 98\%$  were achieved, as determined by GC analysis (Figure 1).



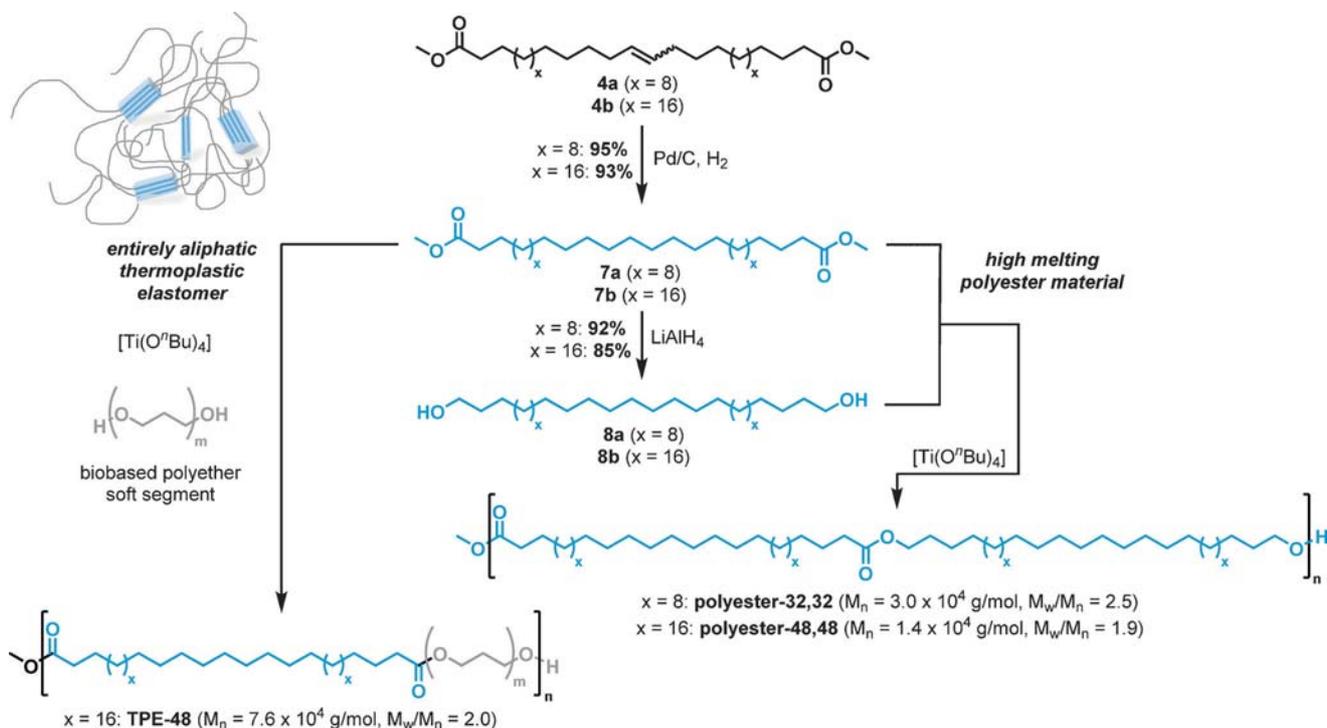
**Figure 1.** GC trace of crude product after “chain doubling” of  $\alpha,\beta$  unsaturated diester **3a** with 2/3 hexenes.

Isolation of the target  $C_{32}$   $\alpha,\omega$  diester was possible by recrystallization to yield an overall 86 % of **4a** in a purity greater than 99 %, as determined by GC analysis (Supporting Information, Figure S24).

To access even longer chains, we employed erucic acid (**1b**) as a starting material. The self metathesis and subsequent esterification in methanol of this  $C_{22}$  unsaturated fatty acid yields an internally unsaturated  $C_{26}$   $\alpha,\omega$  diester.  $C_{26}$  diester **2b** can be used in a double bond isomerization for the preparation of  $\alpha,\beta$  unsaturated diester **3b**. As the hydrocarbon segment of diester **2b** is significantly longer as compared to the segment of diester **2a** from oleic acid, in the isomerization equilibrium the  $\alpha,\beta$  unsaturated isomer is present to a lesser extent of 6.7 % ( $E/Z = 57$ ).

As an additional effect of the longer chain, the decreased solubility of the compound has to be overcome in a dynamic isomerizing crystallization. Here, working in ethanol led to a crude yield of 95 % with a selectivity for **3b** of 63 %. The pure compound, isolated in 57 % yield after recrystallization, can be chain doubled to  $C_{48}$   $\alpha,\omega$  diester **4b** via the two step, one pot process described above. The desired ultra long chain diester could be obtained in 92 % in a purity greater than 99 %, as determined by GC analysis (see the Supporting Information).

As a further demonstration of the utility, reactivity, and purity of the ultra long chain  $\alpha,\omega$  diesters, saturated analogues, corresponding diols and a polyester, were generated (Scheme 3). Saturated diesters **7a** and **7b** were prepared by hydrogenation of **4a** and **4b** using Pd/C and hydrogen. The diesters were obtained in 95 and 93 % respectively, in polymerization grade purity as determined by GC (Supporting Information, Figures S26 and S27). Corresponding diols **8a** and **8b** were synthesized by reduction of the ester moieties



**Scheme 3.** Preparation of polymeric materials composed of aliphatic ultra long chain monomers.

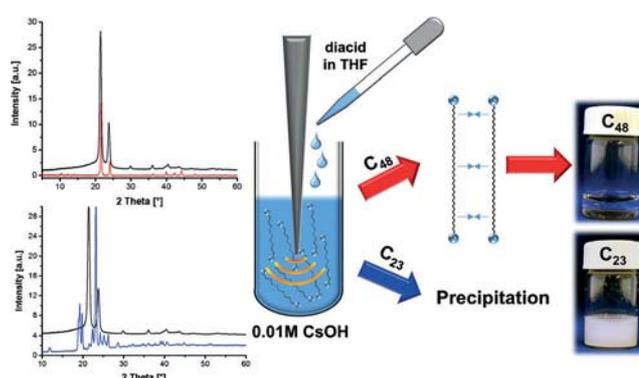
using  $\text{LiAlH}_4$  in 92 % and 85 % yield, respectively. With these compounds accessible in pure form on a multigram scale, we prepared polyesters **32,32** and **48,48** in a melt polycondensation using titanium(IV) tetrabutoxide ( $[\text{Ti}(\text{O}^i\text{Bu})_4]$ ) as a transesterification catalyst (Supporting Information, Table S3). The influence of the long aliphatic polymethylene segment of the monomers is reflected in the thermal properties of the polyesters and unprecedented melting temperatures were observed. Whereas polyester **32,32** exhibits a peak melting point of  $T_m = 113^\circ\text{C}$ , the longer analogue polyester **48,48** shows a transition at  $T_m = 120^\circ\text{C}$ . Accordingly, polyester **48,48** is the first aliphatic polyester that clearly surpasses the melting point of low density polyethylene (LDPE), which is an important benchmark value for many applications.<sup>[33]</sup>

A well crystallizable hydrocarbon segment is also crucial for physical cross linking of aliphatic thermoplastic elastomers (TPEs).<sup>[34]</sup> Polycondensation of  $\text{C}_{48}$  diester **7b** and poly(trimethyleneglycol) (PPDO,  $M_n = 3000 \text{ g mol}^{-1}$ ) using  $[\text{Ti}(\text{O}^i\text{Bu})_4]$  as transesterification catalyst yielded an elastomeric material (**TPE-48**, 80 wt % soft segment) with a narrow melting transition ( $T_m = 80^\circ\text{C}$ ). Tensile tests on injection molded samples revealed a good recovery and strength (Young modulus  $E = 9 \text{ MPa}$  and elongation at break  $\epsilon_b = 780\%$ ; see the Supporting Information for complete data). By strong contrast, a material based on  $\text{C}_{23}$  diester and a correspondingly shorter PPDO as a soft phase with an overall similar composition (73 wt % soft segment) possesses a broad melting transition with a peak at only  $T_m = 39^\circ\text{C}$ , which could not even be injection molded on account of the low crystallization temperature and crystallinity.<sup>[35]</sup> This underlines the ability of the ultra long chain units to function as a crystallizable block in block copolymers. The aforementioned mechanical properties of **TPE-48** also compare favorably to those of commercial thermoplastic polyester elastomers.<sup>[36]</sup>

This observation of a high crystalline order encourages a study of the self assembly properties of the ultra long chain compounds. To this end, we synthesized  $\text{C}_{48}$  dicarboxylic acid **9** with two more hydrophilic carboxylate moieties by saponification of diester **7b** with KOH in THF. Notably, WAXS of **9** as a bulk material already revealed the characteristic orthorhombic polyethylene structure. This differs from the behavior of shorter analogues, as for example  $\text{C}_{23}$  dicarboxylic acid **10** (available from isomerizing alkoxyacylation of erucic acid),<sup>[37]</sup> which pack into a different crystal structure (Figure 2).

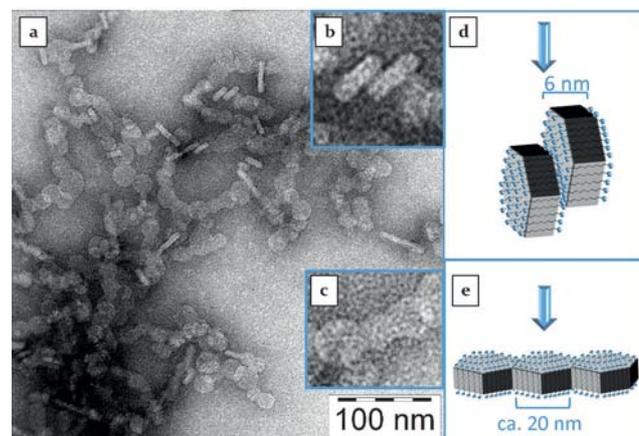
To study the self assembly to nanostructures, dicarboxylic acids **9** and the  $\text{C}_{23}$  analogue **10** for comparison were dissolved in hot THF and injected in a 0.01M aqueous CsOH solution under ultrasonication. In contrast to  $\text{C}_{23}$  diacid **10**, which formed macroscopic precipitates directly upon addition,  $\text{C}_{48}$  diacid **9** leads to the formation of a clear transparent dispersion (Figure 2). Dynamic light scattering (DLS) revealed the presence of particle with sizes around 6–7 nm with a rather narrow size distribution of  $\text{PDI} = 0.22$ .

We believe that the precise ultra long polymethylene sequence acts as a strong driving force for crystallization leading to the formation of crystalline nanoparticles. These particles are stabilized by the hydrophilic interaction of the



**Figure 2.** WAXS of semi crystalline polyethylene (black),  $\text{C}_{48}$  dicarboxylic acid **9** (red), and  $\text{C}_{23}$  dicarboxylic acid (blue); self assembly behavior of ultra long chain dicarboxylic acid **9**, and  $\text{C}_{23}$  dicarboxylic acid **10** for comparison, in aqueous CsOH solution.

ordered COOH groups with the surrounding medium. Astoundingly, transmission electron microscopy (TEM) revealed anisotropic shapes resembling the hexagonal structure of typical crystalline polyethylene nanoparticles (Figure 3).<sup>[38]</sup> The crystal thickness was determined from particles oriented parallel to the electron beam, yielding a value of 6 nm. This thickness corresponds to the length of the fully extended  $\text{C}_{48}$  dicarboxylic acid and supports the single layer, extended chain nature of the formed nanocrystals (Figure 3 d,e).



**Figure 3.** TEM images of stained (1% phosphotungstic acid)  $\text{C}_{48}$  nanoparticles: a) overview; section with particles b) parallel and c) perpendicular to the electron beam; d,e) representations of (b) and (c). The blue arrows indicate the direction of the electron beam.

In summary, we show how the methylene chains of two fatty acid molecules can be linked to form an ultra long chain product. This provides access to  $\alpha,\omega$  difunctional products with chain lengths that bear potential in many instances, but have not been accessible to date. Readily available unsaturated fatty acids serve as a starting material. Our approach comprises catalytic steps exclusively, namely olefin isomerization, crystallization and olefin metathesis, which are all proven to be suited for large scales.<sup>[21,39]</sup> As the only co

reagents, short chain olefins which are waste products of the petroleum industry and furthermore can be recycled are required. Almost the entire starting material is incorporated in the product, and the small amount of short chain esters formed can also be useful materials. In principle, the procedure can be iterative as the chain doubled product can serve as the starting material for another cycle of isomerization/crystallization and metathesis. The potential and unique properties of these new building blocks are highlighted by derived high melting polyesters, thermoplastic elastomeric block copolymers and self assembled nanocrystals. Particularly the latter two cases reveal the special ability of the ultra long  $C_{48}$  entity to crystallize in a polyethylene like fashion. This clearly differs from shorter analogues, corresponding to only the length of one fatty acid chain. In this sense, the compounds accessible through the “chain doubling” approach can be regarded as polyethylene telechelics<sup>[19,40]</sup> with an absolutely precise chain length and end group fidelity.

### Experimental Section

General procedure for the synthesis of  $\alpha,\beta$  unsaturated diesters **3a** and **3b**: In a typical experiment, a 1 L round bottom flask with a nitrogen inlet was charged with 25.00 g of diester **2a** or **2b** that were degassed and subsequently dissolved in 900 mL of dry alcohol. The solution was cannula transferred into a 1 L double walled glass reactor with a magnetic stirring bar attached to a cryostat. 0.5 mol % of isomerization catalyst **Cat2** dissolved in 5 mL of the corresponding alcohol were added to the solution, and the reactor was closed and stirred at 250 rpm. By means of the cryostat, the reactor was cooled (0.25 K min<sup>-1</sup>) to a temperature where the solution became cloudy due to the formation of initial crystals (typical clouding temperature for **2a**: 6–10°C; for **2b**: 26–30°C). Subsequently, the reaction was cooled to the final temperature over the course of the designated time (Supporting Information, Figures S2 and S9). Upon reaching this temperature, the isomerization was quenched by the addition of 5 mL of triethylamine and the slightly yellow precipitate was filtered off. The precipitate was dissolved in a minimal amount of dichloromethane and filtered through a short plug of silica to remove residual catalyst, followed by recrystallization from methanol (in case of **2a**) or heptane (in case of **2b**), respectively, yielding the pure diesters **3a** (70% yield) and **3b** (57% yield) in a purity greater than 99%, as determined by <sup>1</sup>H NMR spectroscopy and GC analysis.

Dimethyl 1,32 dotriacont 16 enedioate (**4a**): In a typical experiment, 10.50 g (30.8 mmol) of  $\alpha,\beta$  unsaturated diester **3a** were degassed in a Schlenk tube. The diester was suspended in 50 mL of dry heptane and 39.25 mL (26.30 g, 312 mmol) of 2/3 hexene. 96.6 mg (154  $\mu$ mol) of **Cat1** and 33.8 mg (0.31 mmol) of 1,4 benzoquinone were dissolved in 1.0 mL of dry dichloromethane and added to the mixture via syringe. The mixture immediately turned dark green and was stirred at 40°C for 20 min. At 30°C, the solvent was removed in vacuo, another 50 mL of dry heptane were added, and the slurry was sonicated for 1 min. Afterwards, the solvent was removed in vacuo, and the mixture was kept at 30°C for 15 min in vacuo. The reaction was quenched by the addition of 10 mL of ethyl vinyl ether and was stirred at room temperature for 5 min. After addition of 20 mL of dichloromethane, the reaction was allowed to stir for further 10 min. The dark green solution was filtered through a short silica plug and washed with dichloromethane. The solvent was removed by rotary evaporation, and the colorless solid was dried in vacuo. After recrystallization from methanol and from heptane ultra long chain diester **4a** was obtained as colorless crystals in 78% (6.47 g,

12.1 mmol) yield in a purity greater than 99%, determined by GC analysis.

Dimethyl 1,48 octatetracont 24 enedioate (**4b**): In a typical experiment, a Schenk flask was charged with 5.00 g (11.0 mmol) of diester **3b** and degassed. 5 mL of dry dichloromethane and 13.87 mL (9.29 g, 110 mmol) of 2/3 hexene were added and the mixture was heated to 40°C. After the diester was dissolved, 34.6 mg (55  $\mu$ mol) of **Cat1** and 11.9 mg (110  $\mu$ mol) of 1,4 benzoquinone were added in 0.5 mL of dry dichloromethane. The solution was stirred for 15 min at 40°C, cooled down to room temperature, and 10 mL of dry heptane were added. Subsequently the volatiles were removed slowly in vacuo. The resulting solid was dissolved in dichloromethane and ethyl vinyl ether was added to quench the reaction. After stirring for 15 min at room temperature the solution was diluted with dichloromethane and filtered through a short silica plug to remove residual catalyst. After recrystallization from heptane, ultra long chain diester **4b** was obtained as colorless crystals in 92% yield in a purity greater than 99%, determined by GC analysis.

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### Conflict of interest

The authors declare no conflict of interest.

**Keywords:** fatty acids · olefin metathesis · polyethylene · double bond isomerization ·  $\alpha,\omega$  difunctional units

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- [27] After removing catalyst residues by filtration over silica, a second isomerization can be conducted upon addition of fresh catalyst. This step can be performed without a significant loss in activity and selectivity and a crude yield of 84% can be obtained with a selectivity for the desired diester **3a** of 83%. Note that this apparently somewhat lower crude yield from the recycled isomers may be due to a higher concentration of residual methyl oleate in the filtrate used as starting material for a second cycle of isomerizing crystallization.
- [28] Note that performing a self metathesis of  $\alpha,\beta$  unsaturated diester **3a** under reduced pressure at elevated temperatures resulted in isomerization of the double bond, leading to a range of different chain lengths in the self metathesis products with incomplete conversion of the starting material.
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