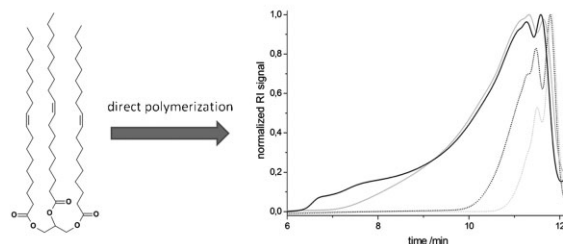


Acyclic Triene Metathesis Oligo- and Polymerization of High Oleic Sun Flower Oil

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High oleic sunflower oil, a renewable raw material consisting of triglycerides with internal C=C-double bonds, was polymerized via acyclic triene metathesis (ATMET) to highly branched and functionalized polyesters. If the Hoveyda–Grubbs second generation catalyst was used and methyl acrylate was introduced as a chain stopper, the molecular weight of the obtained polymers could be tuned by varying the ratio of the triglyceride and methyl acrylate. Using the first generation Grubbs catalyst for the polymerization of high oleic sunflower oil, no cross-linking was observed, even without the use of a chain stopper. The resulting branched materials were characterized by GPC, ^1H and ^{13}C NMR, and ESI-MS.



renewable resource: high oleic sunflower oil → direct polymerization → hyperbranched polyesters

Introduction

Fats and oils are the most important renewable feedstock of the chemical industry.^[1] They are increasingly used for the production of monomers, and can also directly be polymerized.^[2] Moreover, unsaturated fatty compounds are well suited renewable raw materials for olefin metathesis reactions.^[3] Pioneering work of Boelhouwer and coworkers^[4] on olefin metathesis with unsaturated fatty acid derivatives was for instance further developed by Warwel et al.^[5,6] Nowadays, metathesis is becoming an important reaction in oleochemistry that allows the synthesis of monomers for the production of polymers such as polyesters, polyamides, polyethers, and functionalized

polyolefins.^[7] An important advance for all metathetic conversions was the introduction of homogeneous ruthenium catalysts by Grubbs (Grubbs I: ref.^[8] Grubbs II: ref.^[9]). In the field of oleochemistry, long chain dicarboxylic acid esters were prepared by self-metathesis of, e.g., methyl 10-undecenoate using the first generation Grubbs catalyst at concentrations of 0.01 mol-% Ru.^[10] High conversions of 74–82% were obtained for these transformations. Current investigations of cross-metathesis reactions of unsaturated fatty acid methyl esters with methyl acrylate (MA) show that Grubbs and second generation Hoveyda–Grubbs catalysts are very efficient to give the respective α,ω -diesters.^[11] Remarkably, the cross-metathesis of methyl 10-undecenoate and acrylonitrile using Hoveyda–Grubbs second generation catalysts was reported to give methyl 11-cyano-10-undecenoate, which could be hydrogenated with the same catalyst to give the saturated methyl 11-cyanoundecanoate.^[12] Moreover, metathesis reactions that are performed directly with commercially available unsaturated plant oils are of great interest. In this respect, Larock and coworkers developed a solvent free process for the acyclic diene metathesis (ADMET) of vegetable oils in the presence of the first generation Grubbs catalyst in quite low concentrations of 0.1 mol-%.^[13] The ADMET polymerization

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was applied to soybean oil giving polymeric materials ranging from sticky oils to rubbers, while the corresponding reaction of glyceryl trioleate proceeded first by formation of monocyclic oligomers as main products, which subsequently cross-linked.^[14] Recently, the acyclic triene metathesis (ATMET) reaction of the unsaturated model triglyceride glyceryl triundec-10-enoate **1** (Figure 1) was reported.^[15] It was observed that it is possible to control the molecular weight of the resulting branched macromolecules by the application of MA as chain stopper for this straightforward one step one pot polymerization, giving functionalized materials with methyl carboxylate end groups. The best results concerning reaction conditions and yields were obtained using the second generation Hoveyda–Grubbs catalyst.

Therefore, it seems to be self-evident to apply the ATMET reaction with MA as chain stopper to naturally occurring triglycerides, such as high oleic sunflower oil **2**. High oleic sunflower oil is a commercially available native oil containing >90% oleic acid with an internal (*Z*)-configured C=C double bond. In analogy to the reaction of **1** and MA, initiated by Grubbs- and Hoveyda–Grubbs-catalysts, oligo- and polymers can be expected from the respective reaction of **2** depending on the amount of MA used (Figure 2). Within the present contribution, we focused not only on the characterization of the obtained oligo- and polymers but also on the isolation and characterization of some low molecular intermediates of the ATMET reactions via ESI-MS.

Experimental Part

Analytical Equipment

¹H and ¹³C NMR spectra were recorded in CDCl₃ on a Bruker DRX 500 spectrometer at 20 °C. Chemical shifts are given in ppm relative to TMS ($\delta = 0.00$ ppm). ESI-MS experiments were performed using a

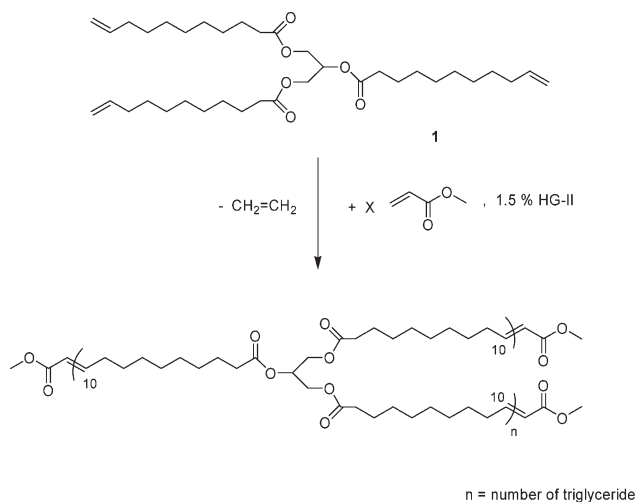


Figure 1. Acyclic triene metathesis (ATMET) polymerization of glyceryl triundec-10-enoate **1** with MA as chain stopper.^[15]

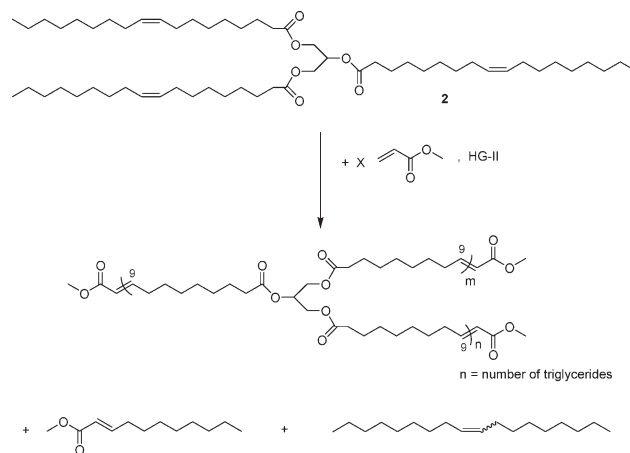


Figure 2. Acyclic triene metathesis (ATMET) polymerization of high oleic sunflower oil **2** with MA as chain stopper.

Finnigan LCQ (Thermo Finnigan, San José, CA, USA) quadrupole ion trap mass spectrometer equipped with a standard electrospray ion source, which was used with a stainless steel metal capillary (110 μm id, 240 μm od, 120.5 mm of length, Metal Needle Kit, Thermo Finnigan). LiClO₄ was added to the analyte to obtain the lithiated molecular ions $M\text{-Li}^+$. A Micromass Premier quadrupole-time of flight (Q-ToF) instrument (Waters, Manchester) equipped with an ESI ion source containing a stainless steel metal spray capillary (127 μm inner diameter, 229 μm outer diameter, 181 mm of length) was used for some ESI-MS/MS experiments.

All products were unambiguously identified by ¹H and ¹³C NMR and by ESI-MS. ¹H NMR data of the crude product mixtures were used to calculate the degree of polymerization.

Polymer molecular weights were determined using an SEC system LC-20A from Shimadzu equipped with an SIL-20A autosampler, PL gel 5 μm Mixed-D column (Polymer Laboratories, 300 mm \times 7.5 mm), and an RID-10A refractive index detector. THF was used as the eluent (flow rate 1 mL \cdot min⁻¹) at 50 °C. All determinations of molar mass were performed relative to linear poly(methyl methacrylate) standards (Polymer Standards Service, M_p 102–981.000 Da).

Thin layer chromatography (TLC) was performed on silica gel TLC cards (layer thickness 0.20 mm, Merck). Compounds were visualized by 2 *N* sulfuric acid/heat. Silica gel 60 (070–230 mesh, Merck) was used for column chromatography.

Analytical GC was performed on a Carlo–Erba GC series 4160 with an FID detector and fused-silica capillary column DB1, 29 m, and GC-MS with a Finnigan MAT 95.

Kugelrohr distillation apparatus was purchased from Büchi Labortechnik AG, Flawil, Switzerland.

Reagents

High oleic sunflower oil (91.2% oleic acid, 3.0% palmitic acid, 2.8% linoleic acid, and 1.9% stearic acid) **2** was purchased from T + T Oleochemie GmbH, 63755 Alzenau, Germany. [1,3-Bis-(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro(*o*-isopropoxyphenylmethylene)ruthenium (second generation Hoveyda–

Grubbs catalyst, HG-II), benzylidene-*bis*-(tricyclohexylphosphin)-dichlororuthenium (first generation Grubbs catalyst, G-I), benzylidene[1,3-*bis*(2,4,6-trimethylphenyl)-2-imidazolidinylidene] dichloro (tricyclohexylphosphine)ruthenium (second generation Grubbs catalyst, G-II), ethyl vinyl ether (99%) and MA (99%) were obtained from Aldrich and used without further purification.

Acyclic Triene Metathesis (ATMET) Reaction of High Oleic Sunflower Oil with Methyl Acrylate (MA) as Chain Stopper (General Procedure)

A mixture of high oleic sunflower oil **2** (0.5 g, 0.56 mmol) and the respective amount of MA in a round bottom flask was degassed and then flushed with nitrogen (2 freeze–thaw cycles). After addition of HG-II (4.8 mg, 1.4 mol-%, 0.0077 mmol), the sample was heated in nitrogen atmosphere to 70 °C and stirred for 2 h. Then the sample was subjected to Kugelrohr distillation (80 °C, 5×10^{-3} mbar) to continuously remove 9-octadecene and methyl 2-undecenoate from the reaction mixture. When no further distillation of low molecular weight products was observed (about 2 h), the reaction was stopped by addition of ethyl vinyl ether. The excess ethyl vinyl ether was removed in vacuo. The obtained crude reaction product was used directly for GPC and NMR analysis. 9-Octadecene and methyl 2-undecenoate were identified in the distillate by GC-MS. The ATMET reaction of **2** and MA was carried out using ratios of 1:7, 1:5, 1:3, 1:2, and 1:1. A further reaction was performed without MA giving insoluble products. Some reactions were also performed without Kugelrohr distillation (**2**/MA = 3). An aliquot of the reaction solution of ratio 1:2 was transesterified with methanol catalyzed by sodium methoxide and subsequently analyzed by GC.

Thin layer chromatography (TLC) of crude reaction mixtures was performed using petroleum ether/ether = 1:1 as mobile phase. The spots of the products were directly extracted from the TLC layer using an apparatus and method developed by Luftmann^[16] and transferred online to the ESI mass spectrometer.

Glyceryl Tri-(*E*)-10-methoxycarbonyl-dec-9-enoate (**3**)

Triglyceride **3** was prepared as described in the general procedure of ATMET reaction without the reaction step of Kugelrohr distillation using high oleic sunflower oil (1.5 g, 1.68 mmol), MA (3.0 g, 34.9 mmol), and HG-II (14.4 mg, 1.4 mol-%, 0.023 mmol). After 2 h the reaction was stopped by addition of ethyl vinyl ether and distilled at 80 °C (5×10^{-3} mbar) to remove the by-products. Methyl 2-undecenoate was identified as main product in the distillate by GC-MS. Product **3** was isolated from the distillation residue by column chromatography (silica gel 60, 070–230 mesh) with petroleum ether/ether = 1:1 as an eluent. The fractions containing **3** were collected, the solvent evaporated and the residue dried in vacuo. Yield: 0.77 g (64%), pale yellow oil.

¹H NMR (500.1 MHz, CDCl₃): δ(ppm) = 6.96 (dt, *J* = 16.5, 7.6 Hz, 3 H, 3 × –OOCCH=CH–), 5.82 (d, *J* = 16.5 Hz, 3 H, 3 × –OOCCH=CH–), 5.27 (2 × t, *J* = 6.0 Hz, 1 H, O–CHCH₂–), 4.30 (m, 2 H, 2 × O–CHCH₂–), 4.15 (dd, *J* = 6.0, 12.6 Hz, 2H, –CHCH₂–), 3.72 (s, 9 H, 3 × –OCH₃), 2.31 (t, *J* = 8.2 Hz, 6 H, 3 × –CH₂CO–), 2.20 (dt, *J* = 8.1, 7.6 Hz, 6 H, 3 × –CH₂CH=CH–), 1.62 (m, 6 H,

3 × –CH₂CH₂CO–), 1.47 (m, 6 H, 3 × –CH₂CH₂CH=CH–), 1.30 (m, 20 H, CH₂).

¹³C NMR (125.7 MHz, CDCl₃): δ(ppm) = 173.6(–CH₂–COOCH₂–), 173.2(–CH₂–COOCH–), 167.5(–CH=CH–COOCH₃), 150.0(–CH=CH–CO–), 121.3(–CH=CH–CO–), 69.3(–OCH–), 62.5(CH–CH₂O–), 51.8(–OCH₃), 34.6(–CO–CH₂), 34.4(–CH₂–CH=CH), 32.8, 29.4, 28.3, and 25.2 ppm. MS (ESI-positive): *m/z* = 729 ([M–Li]⁺). In addition to *m/z* 729 (*I* = 100%), *m/z* 687 (*I* = 3%), *m/z* 701 (*I* = 9%), *m/z* 715 (*I* = 9%), *m/z* 743 (*I* = 7%), and *m/z* 757 (*I* = 3%) was detected.

Acyclic Triene Metathesis (ATMET) Reaction of High Oleic Sunflower Oil

High oleic sunflower oil **2** (0.5 g, 0.56 mmol) was degassed in a round bottom flask (2×) and flushed with nitrogen. Then G-I (6.3 mg, 0.0077 mmol, 1.37 mol-%) was added and the sample was subjected to Kugelrohr distillation (80 °C, 5×10^{-3} mbar) to continuously remove 9-octadecene from the reaction mixture. 9-Octadecene was identified in the distillate by GC-MS. The reaction was stopped after 90 min by addition of ethyl vinyl ether. The crude product mixture was analyzed by ¹H and ¹³C NMR spectroscopy, as well as GPC analysis. An aliquot was transesterified with methanol catalyzed by sodium methoxide and analyzed by GC. Another aliquot was hydrogenated with Pd/C. The respective reaction was also performed using G-II and HG-II as a catalyst. Insoluble resins were obtained in the latter cases.

Results and Discussion

The ATMET reaction of high oleic sunflower oil **2** and MA was carried out in the absence of solvent and was catalyzed by the second generation Hoveyda–Grubbs catalyst (HG-II). In our system, we can assume that any cross-metathesis between acrylate and the olefinic double bonds of the oleate of triglyceride **2** (Figure 2) leads to an efficient chain stopping at this reactive site and that polymer growth and branching is solely obtained due to self-metathesis reactions between two oleyl groups. This assumption is based on the fact that internal double bonds are considered as type I olefins, MA as type II olefin and the cross-metathesis products (substituted acrylates) will not participate in metathesis reactions after they are formed.^[17] We used HG-II as a catalyst for these polymerizations, since it is known from literature that it readily catalyzes the cross-metathesis of the electron poor double bond in MA under bulk conditions with low amounts of catalyst^[11] and is suitable for the ATMET polymerization of triglyceride **1** using MA as a chain stopper.^[15] Indeed, by using a high excess of MA, the polymerization of triglyceride **2** was completely suppressed and all internal double bonds of the oleyl groups gave cross-metathesis with MA, thus yielding triglyceride **3** (Figure 3). If the reaction was thus performed with 21 equiv. of MA and a catalyst loading of 1.4 mol-% based on **2**, the highly

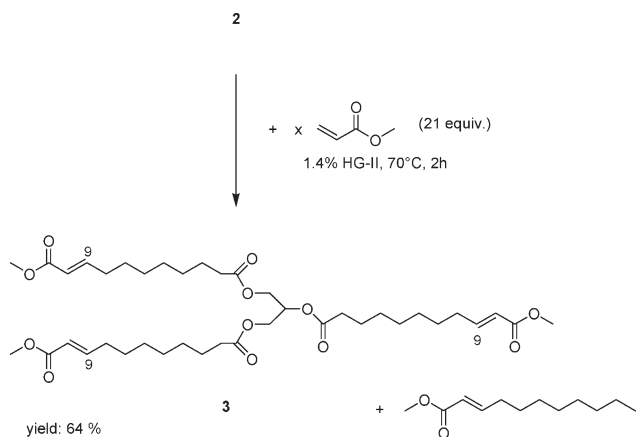


Figure 3. Reaction of high oleic sunflower oil **2** with MA in a ratio of 1:21 giving triglyceride **3** and methyl 2-undecenoate.

functionalized triglyceride **3** was obtained and could be isolated by column chromatography in 64% yield (Figure 3).

No oligo- and polymerization products were detected. Product **3** was characterized by ^1H NMR spectroscopy showing only (*E*)-configured C=C-double bonds ($J = 16.5$ Hz) that are conjugated to carbomethoxy groups. The ^{13}C NMR spectrum showed some minor traces of internal C=C-double bonds, probably resulting from traces of nonreacted oleyl groups or of self metathesis by-products. ESI-MS clearly showed the lithiated molecular ion $\mathbf{3} \cdot \text{Li}^+$ at m/z 729. Thus, the interesting triglyceride **3** can be isolated in good yields and high purity. Structurally, the model compound **3** is very similar to that obtained from the corresponding reaction of glyceryl triundec-10-enoate **1** (Figure 1), however, the alkyl chains of **3** are one methylene group shorter. It has to be pointed out that the synthesis of **3**, which is of interest due to its high functionality and useful for, e.g., the build-up of dendritic architectures, is more convenient because the starting material, high oleic sunflower oil **2**, is a commercially available native oil. Moreover, the low molecular weight by-product, methyl undec-2-enoate, is a valuable starting material for detergent applications and thus only little waste is produced during this reaction.

In further investigations, ATMET polymerizations of **2** were carried out using reduced amounts of the chain stopper MA. Samples with an excess of up to seven equivalents of MA were heated for 2 h at 70 °C and were then subjected to "Kugelrohr" distillation to continue the reaction for an additional 2 h at 80 °C. This procedure was necessary, since the by-product of the self-metathesis of the oleyl groups of **2**, 9-octadecene, it is not easily removed from the reaction mixture. Since olefin metathesis is an equilibrium reaction, the polymerization would be suppressed, if the by-product was not continuously removed from the polymerization mixture (compare Table 1, entry 3 and 4). This problem was thus solved by performing the

Table 1. Characterization of branched macromolecules obtained from metathesis reactions of high oleic sunflower oil **2** and MA (compare also Figure 2).

Entry	[2]/[MA]	E/G^a	\overline{DP}^b	$E:DB^c$	\overline{M}_n^d	PDI ^d
1 ^e)	1:7	2.43	1.4	10 (8.5)	n.d.	n.d.
2 ^e)	1:5	2.32	1.5	4.3 (7)	1 547	1.43
3 ^e)	1:3	1.8	2.5	2 (3)	2 317	1.97
4 ^{e,f})	1:3	2.7	1.2	2.8 (–)	n.d.	n.d.
5 ^e)	1:2	1.27	7.4	1.2 (1.5)	4 986	>20
6 ^e)	1:1.1	1.25	8	1 (1.4)	4 824	16.8
7 ^g)	Pure 2	n.d.	n.d.	n.d.	n.d.	n.d.
8 ^h)	Pure 2	1.45	4.5	0.8 (1.8)	4 695	5.5

^a)Ratio of end groups E (Σ -CH₃, -OCH₃) and glyceryl units G determined by ^1H NMR; ^b)Degree of polymerization of **2** estimated from the ratio $E/G = (\overline{DP} + 2) : \overline{DP}$ (column 3) giving $\overline{DP} = 2 : [(E/G) - 1]$; ^c)Ratio E/DB of end groups E (Σ -CH₃, -OCH₃) and internal double bonds -CH₂CH=CHCH₂- determined by ^1H NMR; in brackets E/DB calculated from \overline{DP} ; ^d)Obtained by GPC; ^e)MA was used as chain stopper in the presence of second generation Hoveyda-Grubbs catalyst; ^f)9-octadecene was not removed by Kugelrohr distillation; ^g)Reaction was performed without MA in the presence of second generation Hoveyda-Grubbs catalyst and yielded cross-linked material; ^h)Reaction was performed without MA in the presence of first generation Grubbs catalyst.

reaction under conditions that allowed the continuous distillation of 9-octadecene from the reaction mixture in vacuo at 80 °C. Using this technique, a further reduction in the amount of MA as a chain stopper in the ATMET reaction mixture led to the formation of branched macromolecules with increased molecular weights, depending on the amount of MA. Ratios of triglyceride **2**/MA of 1:7, 1:5, 1:3, 1:2, and 1:1.1 were used and the results of these investigations are given in Table 1. It is important to mention here, that no precipitation or gelation was observed for the reactions presented in Table 1, with the exception of entry 7. The degree of polymerization (\overline{DP}) was calculated on the basis of the respective ^1H NMR data and was compared to the data obtained by GPC analysis (see Figure 4). Exemplary, ^1H NMR spectra of some of the products presented in Table 1, entries 2, 6, and 7 are given in Figure 5 together with the ^1H NMR spectrum of high oleic sunflower oil **2** for comparison reasons. From the ratio of the intensities of the end groups *E* (-CH₃ and -COOCH₃) and of the glyceryl units *G* (-CH₂O-), which were obtained from the integrals of the corresponding signals in the ^1H NMR spectra of the crude reaction mixtures (0.82 ppm for -CH₃, 3.62 ppm for -COOCH₃, and 4.08 as well as 4.22 ppm for -CH₂O-), the \overline{DP} could be calculated considering that the amount of palmityl (3%) and stearyl (1.9%) groups was about 5% in high oleic sunflower oil **2** (Table 1). In order to

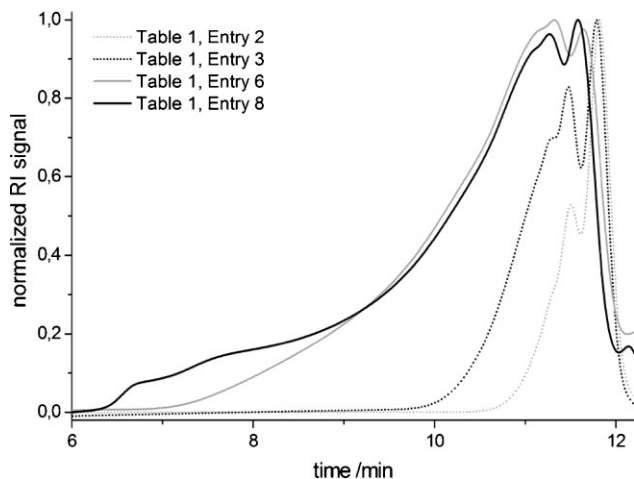


Figure 4. GPC analysis of crude reaction mixtures of high oleic sunflower oil **2** with different amounts of MA.

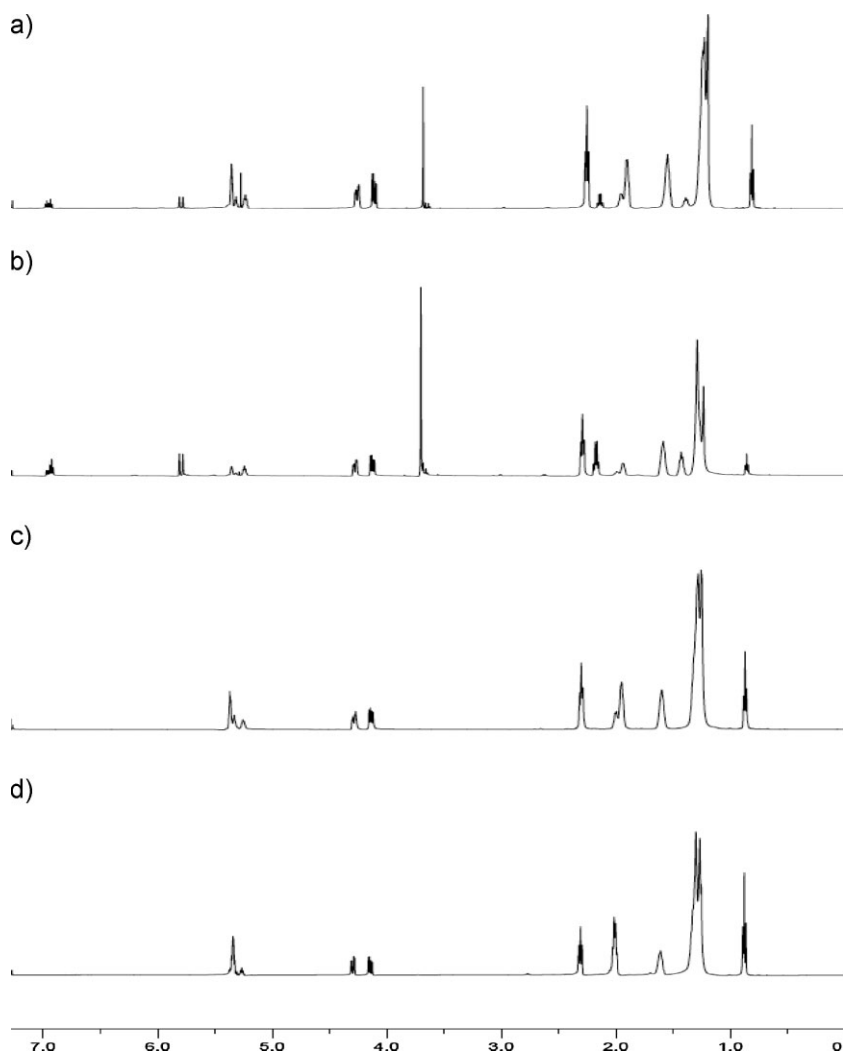


Figure 5. ^1H NMR spectra of products obtained from reactions of high oleic sunflower oil **2** and MA = 1:1.1 (a, see Table 1 entry 6) and 1:5 (b, see Table 1 entry 2), of **2** without MA in the presence of first generation Grubbs catalyst (c, see Table 1 entry 7) and of pure **2** (d).

illustrate this calculation, it is helpful to take an idealized structure of the resulting branched macromolecules (without the possibility of ring-closing, leading to macrocycles) into account. For such idealized macromolecules, the ratio of E/G is approaching 1:1 with increase in molecular weight and the ratio follows the general rule $(x + 2):x$, where x is the \overline{DP} of **2**.

Thus, triglycerides **2** and **3** have of course a ratio $E/G = 3$ (\overline{DP} of **2** = 1). Using a seven-fold excess of MA (Table 1, entry 1) a ratio of $E/G = 2.43$ was observed, corresponding to a \overline{DP} of 1.4. A five-fold excess of MA (Table 1, entry 2) gave a ratio $E/G = 2.32$, which represented a \overline{DP} of 1.5. Consequently, decreasing amounts of MA led to a decrease in E/G ratio and increase in \overline{DP} values (Table 1, entries 3, 4, and 6). As an example to illustrate the importance of 9-octadecene removal, the reaction with a three-fold excess of MA gave a \overline{DP} of only 1.2 when 9-octadecene was not continuously

removed (entry 4), while the respective reaction utilizing the described procedure including Kugelrohr distillation at 80°C resulted in a \overline{DP} of 2.5 (entry 3). The highest \overline{DP} of 8 was obtained with MA and **2** in nearly equimolar amounts (entry 6). When **2** was reacted with second generation Hoveyda–Grubbs catalyst without MA, gelation was observed and insoluble products were obtained due to cross-linking (entry 7). The calculated \overline{DP} on the basis of NMR data of entries 2, 3, and 5 were consistent with the respective average molecular weights (\overline{M}_n), which were obtained by GPC analyses. The GPC data presented in Figure 4 also clearly reveal the discussed correlation between the observed molecular weights and the amount of used chain stopper.

Ring-closing metathesis can be expected during the polymerization of triglyceride **2**, as also reported in the literature for **1**^[15] and for glyceryl trioleate and soybean oil.^[13,14] Indeed, this can be observed by comparison of the experimentally determined ratio of end groups and internal double bonds (E/DB) with the theoretical ratio of E/DB calculated on the basis of \overline{DP} (Table 1, column 4). It is important to note here, that the byproduct, 9-octadecene, was completely removed from the reaction mixture as could be shown by GC analysis. Thus, the formed by-product did not influence that calculated ratios. Generally, the E/DB ratio should follow the rule $E/DB = (x + 2):(x - 1)$ for macromolecules

without macrocycles. However, the measured E/DB ratios are lower than the value that would be expected from \overline{DP} calculations, thus indicating a too high amount of internal double bonds that can be explained by ring-closing reactions (Table 1, column 4). Table 1 entry 6, for instance, shows an experimental ratio $E/DB = 1$. According to the calculated \overline{DP} of 8 for this branched macromolecule, one would expect an E/DB ratio of $(8 + 2):(8 - 1) = 1.4$. The lower experimental ratio of E/DB indicates at least one macrocyclic structure within this branched polymer.

In analogy to the reaction without the chain stopper MA and HG-II, insoluble polymers were also obtained from the reaction of pure **2** catalyzed by second generation Grubbs catalyst G-II. In contrast, when reacting **2** with the first generation Grubbs catalyst G-I, a soluble product with a \overline{DP} of 4.5 equiv. to \overline{M}_n of $\approx 4\,000$ (Table 1, entry 8) was formed. The degree of intramolecular cyclization is even higher for the reaction of pure **2** with G-I having a ratio $E/DB = 0.8$ indicating more than one macrocycle per macromolecule within the macromolecular structure.^[15] This may explain why triglyceride **2** could be polymerized without any cross-linking using G-I catalyst. Intramolecular cyclization and in addition the saturated fatty acids being present in high oleic sun flower oil (5%) may thus prevent cross-linking. Moreover, the G-I catalyst is less reactive for the metathesis of internal double bonds (as present in the prepared polymers,

as well as in the monomer **2**) than G-II and HG-II catalysts.^[18] Therefore, G-I will result in lower functional group conversion and is thus less likely to cross-link the resulting material.

In further studies, we looked in more detail at the formed oligomeric products including the dimers and trimers, which were formed on the way to the polymers. It is interesting that we could detect and identify the important metathesis intermediates **4–6** (Figure 6) as well as dimer **7** and trimer **8** on the way to ATMET polymers using ESI-MS and ESI-MS/MS. Compounds **3–7** were separated by TLC and were then identified by ESI-MS after online extraction from the plates using the method developed by Luftmann.^[16] The crude reaction mixture of **2** and MA in a ratio of 1:5 (Table 1, entry 2) gave besides triglyceride **3** (Figure 3) two monomeric compounds **4** and **5** that were formed by cross-metathesis of one and two oleyl groups of **2** with MA, respectively (Figure 6).

Furthermore, we could identify two dimeric products in this mixture. Dimer **6** resulted from the self-metathesis of compound **5** and dimer **7** was formed by self-metathesis of the starting triglyceride **2**. Products **4–7** could also be identified in the crude reaction mixture using ratios of triglyceride **2** and MA of 1:3 (Table 1, entry 3) and 1:2 (Table 1, entry 5); however, their formation was reduced relative to the formation of polymers compared to the

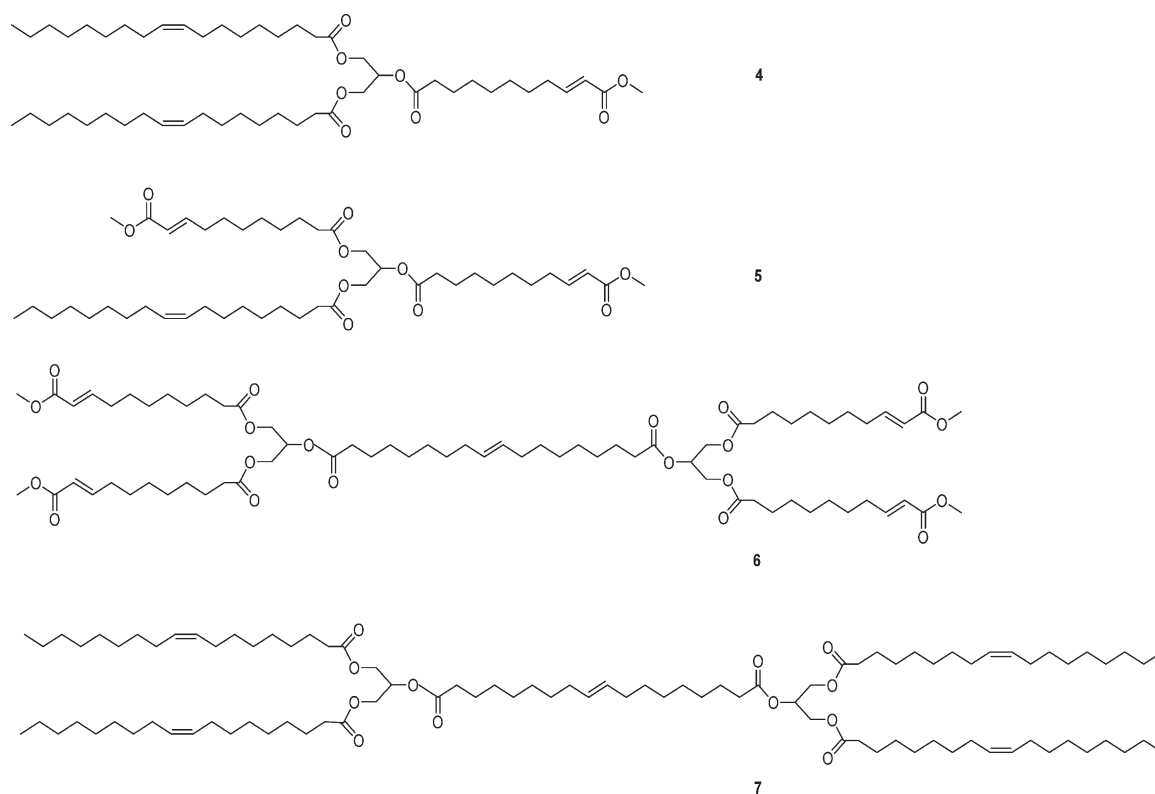


Figure 6. Products **4–7** formed in the ATMET reaction of high oleic sunflower oil (**2**) with MA in a ratio of 1:5.

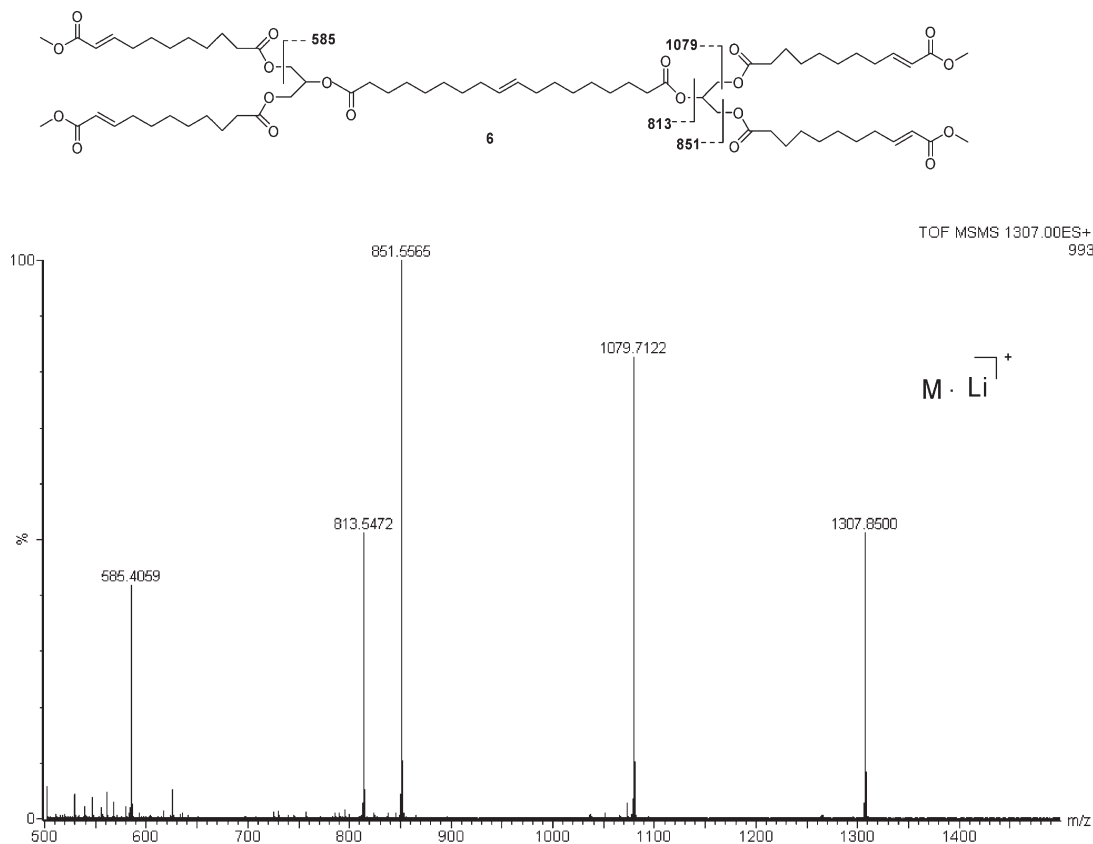


Figure 7. ESI/MS-MS spectrum of dimer **6**. The fragmentation pattern is explained in the structure given above.

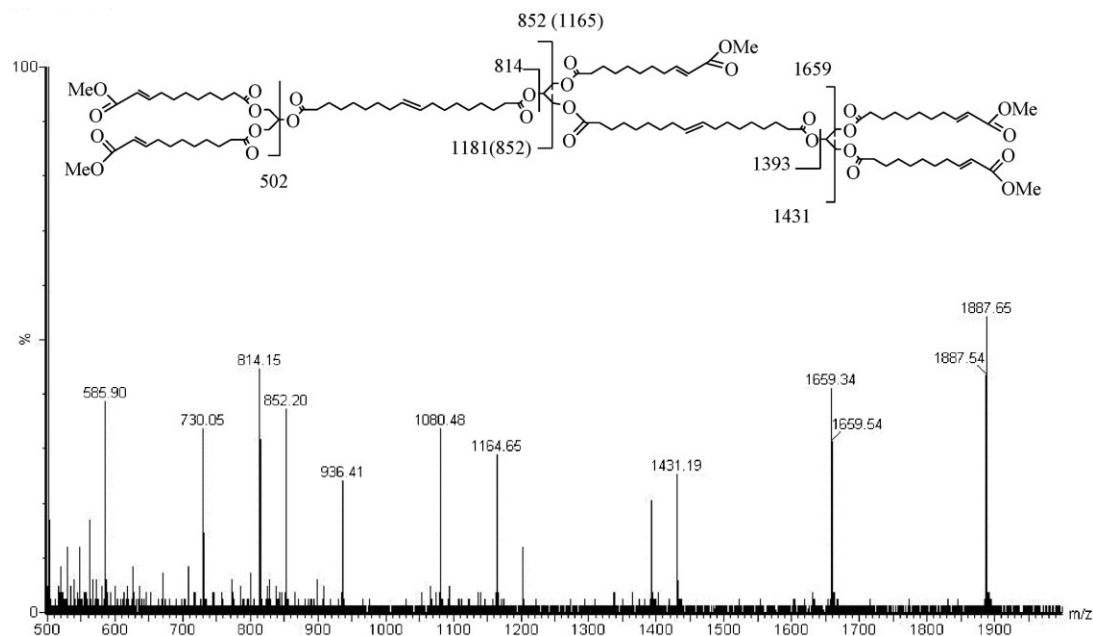


Figure 8. ESI/MS/MS spectrum of trimer **8**. The fragmentation pattern is explained in the formula given above.

reaction with a ratio of 1:5 (Table 1, entry 2). The ESI-spectrum of the reaction presented in Table 1 entry 5 showed inter alia the molecular ion of $[6 \cdot \text{Li}]^+$ at m/z 1307 and the MS/MS-spectrum clearly confirms the structure of **6** as indicated by the fragmentation pattern (Figure 7). By collision induced dissociation (CID) 2-undecenedioic acid monomethyl ester (228 Da) is eliminated as a neutral step by step giving fragments m/z 1079 and m/z 851. Elimination of a diglyceride gives fragment m/z 813 followed by elimination of another equivalent of 2-undecenedioic acid monomethyl ester to give fragment m/z 585 (Figure 7).

Moreover, we could detect trimer **8** by ESI-MS and characterize it unambiguously by ESI-MS/MS of the molecular ion $[8 \cdot \text{Li}]^+$ at m/z 1807 (Figure 8). These ESI investigations clearly reveal that branched oligomeric architectures were formed and clearly identify most of the expected metathesis oligomers that were formed during the initial stage of polymerization. Thus, we can conclude that our ATMET polymerization does indeed lead to branched macromolecules as expected.

The ESI-spectra of compounds **3**, **6**, and **8** showed, in addition to the expected molecular ion of $[M \cdot \text{Li}]^+$, neighboring peaks at an interval of +14 Da, which indicate that side reactions took place under the chosen polymerization conditions.^[19] Moreover, one of the polymer samples (Table 1, entry 5) was transesterified with methanol. The product mixture of the obtained diacids was analyzed by GC-MS revealing dimethyl 9-octadecendioate as main product. However this main product was accompanied by C_{15} – C_{21} diesters (+14 Da) that are formed due to simultaneous olefin metathesis and olefin isomerization side reactions. Based on the studies of Schmidt,^[20] Fokou and Meier discussed in detail the problem of olefin isomerization during ADMET reactions with second generation catalysts, resulting in the observed product distribution with 14 Da mass differences.^[15,19] Thus, if the double bonds are isomerized the resulting new olefin can still participate in self- and cross-metathesis reactions and this leads to different alkyl chain lengths, as observed in the ESI mass spectra, and in the products of transesterification with methanol. We could observe this isomerization in all systems using the HG-II catalyst. ATMET reaction of **2** with G-I catalyst yielded, as expected, the product largely without isomerization.^[19]

Interestingly, the molecular weights obtained for triglyceride **2** are similar to the molecular weights obtained for ATMET polymerization of triglyceride **1**, whereas the polydispersity index (PDI) is significantly larger. One possible explanation for this behavior might be the similar rate constants of self-metathesis of internal double bonds (as present in compounds **2** as well as in, e.g., the dimer **6**, the trimer **8**, and higher oligomers), whereas in the case of triglyceride **1** the rate constant of self-metathesis of the

terminal double bonds is higher than that of internal double bonds.^[21] Therefore, polymerization is favored over secondary metathesis reactions for monomer **1**, if compared to monomer **2**.

Conclusion

The ATMET reaction with MA as chain stopper was applied to high oleic sunflower oil as an example of a native oil to produce highly branched polyesters in a solvent free one step reaction. The ratio between the triglyceride as monomer and MA as chain stopper was used to tune the molecular weight of the prepared macromolecules. The products could be characterized by NMR, GPC, and especially ESI-MS thus confirming their branched structure. The highly unsaturated polyesters containing acrylic end groups as well as internal C,C-double bonds are interesting reactive products obtainable from plant oils as a renewable raw material.

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