Research Article

Cross-metathesis of unsaturated triglycerides with methyl acrylate: Synthesis of a dimeric metathesis product

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Highly functionalized dimeric triglycerides, such as compound **2**, are obtained as minor products besides branched macromolecules from the acyclic triene metathesis (ATMET) polymerization of unsaturated triglycerides such as glyceryl triundec-10-enoate **1** and methyl acrylate (MA) in the presence of the second generation Hoveyda–Grubbs catalyst. The formed amount of interesting products of lower molecular weight during the ATMET reaction depends on the ratio of MA and triglyceride, reaction time, and temperature. We isolated the dimeric metathesis product **2** and synthesized the respective partially hydrogenated dimer **3** regioselectivly in a seven step reaction sequence starting from 10-undecenoic acid **7** and glycerol. Product **3** was unambiguously characterized by ^{13}C and ^{1}H NMR and MS as well as the further intermediate products of the seven step reaction including 10,11 bromo-undecanoic acid **8**, the respective brominated 1,3-diglyceride **9**, the brominated 1,3-triglyceride **6**, and the self-metathesis products **4** and **5** which were isolated and purified.

Keywords: Highly functionalized dimeric triglycerides / Olefin self- and cross-metathesis / Renewable resources

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1 Introduction

Fats and oils are the most important renewable feedstock among renewable raw materials, which are currently used by the chemical industry [1–3]. Especially unsaturated fatty compounds are of great interest. They are used for, *e.g.*, metathesis reactions that allow the synthesis of polymers such as polyesters, polyamides, and polyethers from suitable monomers, and of functionalized polyolefins becoming more and more important in oleochemistry [4]. Recently, the acyclic triene metathesis (ATMET) reaction of unsaturated triglycerides, such as high oleic sunflower oil [5] and glyceryl triundec-10-enoate **1**, which was synthesized from 10-undecenoic acid and glycerol, was described to give highly functionalized and branched polymers (Fig. 1) [6].

The reaction was carried out with methyl acrylate (MA) as chain stopper catalyzed by the second generation Hoveyda–Grubbs catalyst – HG-II). On the way to the polymers also lower molecular weight products such as the dimers **2** (Fig. 2)

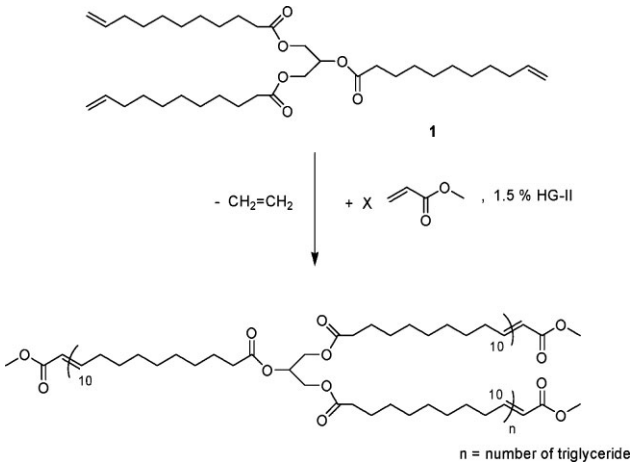

Figure 1. ATMET of glyceryl triundec-10-enoate **1** with MA as chain stopper [6].

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Abbreviations: ATMET, acyclic triene metathesis; **HG-II,** second generation Hoveyda–Grubbs catalyst; **MA,** methyl acrylate.

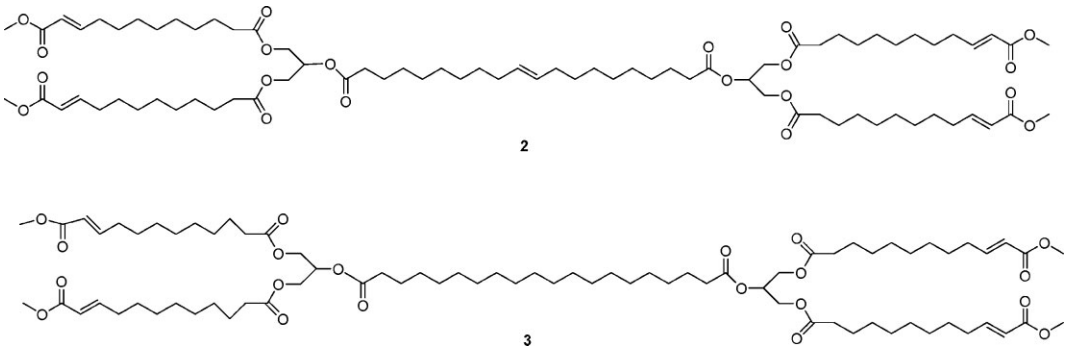

Figure 2. Di-triglyceride **2** is formed as dimeric product (DP = 2), Fig. 1, in the ATMET reaction of glyceryl triundec-10-enoate **1** with high excess of MA as chain stopper. Selective hydrogenation of the internal C,C-double bond of **2** gives compound **3**.

and trimers were formed depending on the ratio of MA and triglyceride **1**, time, and temperature. Di-triglyceride **2** was one of the lower molecular compounds that was isolated by liquid chromatography and characterized by NMR and ESI/MS. It can be expected that a mixture of regioisomeric self-metathesis products like dimer **2** containing the diacid ester bonds in 2,2′-position of glycerol as well as 1,1′- and 1,2′-position was formed.

The question was if it is possible to isolate the highly functionalized cross- and self-metathesis product **2**, and to synthesize **2** or compound **3** regioselectivly by independent synthesis to have reference materials for a better characterization of the formed oligomeric mixtures. The retrosynthesis of di-trigyceride **3**, as shown in Fig. 3, let expect that *tetra*-bromo triglyceride **6** would be a suitable substrate to start the synthesis.

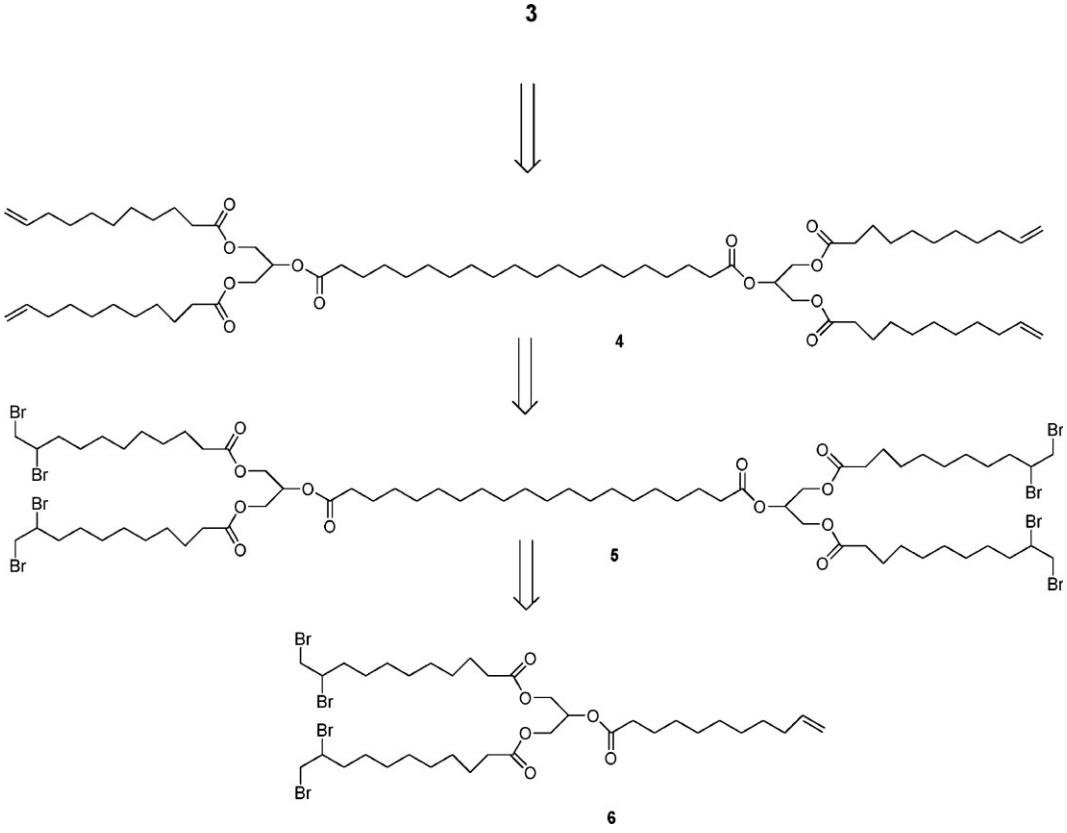

Figure 3. Retrosynthesis of di-triglyceride **3** using partially brominated glyceryl triundec-10-enoate **6** as starting material.

2 Materials and methods

2.1 Analytical equipment

Analytical GC was performed on a Carlo Erba GC series 4160 with an FID detector and fused silica capillary column DB1, 29 m. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker DRX 500 spectrometer at 20°C using TMS (^{1}H NMR) and $CDCl_3$ ($\delta = 77.0$ ppm, ^{13}C NMR) as internal standards. CI-Mass spectra were recorded on a Finnigan MAT 95. ESI-MS experiments were performed using a Finnigan LCQ (Thermo Finnigan, San José, CA) quadrupole ion trap mass spectrometer equipped with a standard electrospray ion source, which was used with a stainless steel metal capillary (110 μm inner diameter, 240 μm outer diameter, 120.5 mm of length, Metal Needle Kit, Thermo Finnigan). The high-resolution experiment of compound **2** was performed using a Micromass Premier quadrupole-TOF (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).

All products were unambiguously identified by ^{1}H and ^{13}C NMR, and by CI-MS. 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. Kugelrohr distillation apparatus was purchased from Büchi Labortechnik AG, Flawil, Switzerland.

2.2 General

10-undecenoic acid (97%) **7** was obtained from Atochem, France, and used without further purification as well as MA (99%) and ethyl vinyl ether (99%), which were purchased from Aldrich. Benzylidene [1,3-*bis*-(2,4,6-trimethylphenyl)-2 imidazolidinylidene] dichloro (tricyclohexylphosphine)ruthenium (second generation Grubbs catalyst, G-II) and [1,3-*bis*-(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro(*o*-isopropoxy-phenylmethylene)ruthenium (HG-II) were obtained from Aldrich.

2.3 Glyceryl triundec-10-enoate 1

10-undecenoic acid **7** (100 g, 542.5 mmol), glycerol (14.16 g, 153.8 mmol) and *p*-toluenesulfonic acid (1.54 g, 8.11 mmol) were heated in xylene (150 mL) under reflux in a nitrogen atmosphere using a dean stark apparatus for efficient water removal for 24 h. Then the solvent was removed *in vacuo* and the residue was dissolved in petroleum ether (400 mL). After addition of sodium bicarbonate (200 mL) the solution was heated under reflux for 1.5 h. The layers were separated and the organic layer was washed with H_2O until no 10-undecenoic acid **7** was detectable (TLC). The organic layer was dried with Na_2SO_4, filtered and the solvent was evaporated *in vacuo*. After column chromatography of the crude product (silica gel, petroleum ether/diethyl ether = 8:2) fractions containing triglyceride **1** were collected, the solvent evaporated and the residue dried *in vacuo*. Yield: 87.2 g (78.5%). Triglyceride **1** was characterized by ^{1}H and ^{13}C NMR spectroscopy; the data of the ^{1}H NMR spectrum correspond to those given in the literature [6].

^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta = 173.7$ (2× CO), 173.2 (1× CO), 139.5 (*C*H=CH_2), 114.6 (CH=*C*H_2), 69.3 (CHO), 62.5 (2× CH_2O), 34.6–34.2, 29.7–29.3, 25.3 ppm.

2.4 ATMET reaction of glyceryl triundec-10-enoate 1 with methyl acrylate and isolation of dimeric metathesis product 2

A mixture of glyceryl triundec-10-enoate **1** (5.0 g, 8.45 mmol) and MA (2.2 g, 25.34 mmol) in a round bottom flask was degassed and then flushed with nitrogen (two freeze-thaw cycles). After addition of HG-II (80 mg, 0.13 mmol), the sample was heated under nitrogen atmosphere to 75°C, stirred for 5 h, and the reaction was then stopped by addition of ethyl vinyl ether. Excess of ethyl vinyl ether was removed *in vacuo*, the residue dissolved in dichloromethane (150 mL) and stirred with silica gel (15 g) for 1 h at RT. After filtration and evaporation of the solvent 3.6 g of crude product were obtained and subjected to column chromatography (silica gel) using petroleum ether/diethyl ether = 1:1 as eluent. Fractions containing dimer **2** were collected, the solvent evaporated and the residue dried *in vacuo*. Yield: 0.22 g (3.8%). High-resolution-ESI-MS: $C_{78}H_{128}O_{20}Li$ calcd.: 1391.9159; found: 1391.9135.

^{1}H NMR (500.1 MHz, $CDCl_3$): $\delta = 6.98$ (dt, $\mathcal{J} = 16.0$, 7.4 Hz, 4H, C*H*=CHCO), 5.84 (dd, $\mathcal{J} = 16.0$, 1.2 Hz, 4H, CH=C*H*CO), 5.39 (m, 2H, CH_2CH=C*H*CH_2), 5.28 (m, 2H, CHO), 4.31 (dd, $\mathcal{J} = 12.4$, 4.8 Hz, 4H, CH_2O), 4.17 (dd, $\mathcal{J} = 12.4$, 6.2 Hz, 4H, CH_2O), 3.74 (s, 12 H, OCH_3), 2.33 (t, $\mathcal{J} = 8.2$ Hz, 4H, CH_2CO), 2.32 (t, $\mathcal{J} = 8.0$ Hz, 8H, CH_2CO), 2.23 (dt, $\mathcal{J} = 8.1$, 7.7 Hz, 8H, C*H*$_2$CH=CH), 1.98 (m, 4H, C*H*$_2$CH=CHC*H*$_2$), 1.64 (m, 12H, $COCH_2CH_2$), 1.47 (m, 8H, CH_2), 1.31 (m, CH_2). ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta = 173.2$ (4× CO), 172.8 (2× CO), 167.1 (4× CO), 149.6 (COCH=*C*H), 130.3 (CH=CH), 120.9 (CO*C*H=CH), 68.9 (2× OCH), 62.1 (4× OCH_2), 51.3 (OCH_3), 34.2–34.0 (6× CH_2CO), 32.6–32.2 (4× *C*H_2CH=CH_2 and *C*H_2CH=CH*C*H_2), 29.7–28.9 (CH_2), 28.0, 24.8 (6× *C*H_2CH_2CO) ppm. MS (ESI-positive): $m/z = 1408$ ([M Na]$^+$).

2.5 10,11-Dibromoundecanoic acid 8

After cooling of a solution of 10-undecenoic acid **7** (50.0 g, 271 35 mmol) in 250 mL CH_2Cl_2 (0°C) 43.55 g of bromine (13.95 mL, 272.5 mmol) dissolved in CH_2Cl_2 (80 mL) were added dropwise (ice bath) until the mixture did not become

discolored. Then the mixture was washed with sodium sulfite solution (2 mL × 100 mL) and H_2O (2 mL × 150 mL). After further washing with NaCl-solution (100 mL), necessary because of poor separation of the layers, the organic layer was separated, dried with $NaSO_4$, filtered, and the solvent was evaporated *in vacuo*. Yield: 88.5 g (95.0%).

^{1}H NMR (500.1 MHz, $CDCl_3$): $\delta = 4.16$ (dddd, $J = 10.0$, 4.5, 4.0,1.6 Hz, 1H, CHBr), 3.84 (dd, $J = 10.0$, 4.5 Hz, 1H, $CH_{a,b}Br$), 3.63 (dd, $J = 10.0$, 10.0 Hz, 1H, $CH_{a,b}Br$), 2.35 (t, $J = 7.5$ Hz, 2H, CH_2CO), 2.13 (m, 1H, $CHBrCH_{a,b}$), 1.78 (m, 1H, $CHBrCH_{a,b}$), 1.63 (tt, $J = 7.5$, 7.4 Hz, 2H, CH_2CH_2CO), 1.56 (m, 1H, $CHBrCH_2CH_{a,b}$), 1.44 (m, 1H, CHBr–CH_2–$CH_{a,b}$), 1.23 (m, 9H, CH_2). ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta = 180.1$ (CO), 53.04 (C1), 36.3 (C9), 36.0 (C11), 34.0 (C2), 29.1 (C6), 29.0 (C5 and C4), 28.7 (C7), 26.7 (C3), 24.6 (C8) ppm.

2.6 1,3-(10,11 Dibromoundecanoyl)diglyceride 9

10,11-Dibromoundecanoic acid **8** (5.0 g, 14.53 mmol), glycerol (0.54 g, 5.81 mmol) and *p*-toluenesulfonic acid (0.041 g, 0.22 mmol) were heated in xylene (20 mL) under reflux using a dean stark apparatus for 8 h. Then the solvent was removed *in vacuo* and the residue was dissolved in diethyl ether and heated under reflux for 1 h with sodium bicarbonate. After washing with H_2O (3 mL × 30 mL) the organic layer was dried with Na_2SO_4, filtered and the solvent was evaporated *in vacuo*. The crude product was applied to column chromatography (silica gel) using petroleum ether/ethyl acetate = 6:4 as eluent for separation of the product mixture. The fractions containing 1,3-diglyceride **9** were collected, the solvent evaporated, and the residue dried *in vacuo*. Yield: 1.3 g (24.1%).

^{1}H NMR (500.1 MHz, $CDCl_3$): $\delta = 4.18$ (m, 6 H, 2× CHBr and 2× CH_2O), 4.08 (m, 1H, CHO), 3.84 (m, 2H, 2× $CH_{a,b}Br$), 3,64 (2× dd, $J = 11.0$, 11.0 Hz, 2H, 2× $CH_{a,b}Br$), 2.87 (1H, OH), 2.35 (t, $J = 7.5$ Hz, 4H, 2× CH_2CO), 2.14 (m, 2H, 2× $CHBrCH_{a,b}$), 1.82 (m, 2H, 2× $CHBrCH_{a,b}$), 1.64 (m, 4H, 2× $COCH_2CH_2$), 1.57 (m, 4H), 1.44 (m, 2H), 1.32 (m, 18H, CH_2). ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta = 173.1$ (2× CO), 68.3 (CHOH), 65.0 (2× CH_2O), 53.0 (2× CHBr), 36.3 (2× CH_2CHBr), 36.0 (2× CH_2Br), 34.0 (2× CH_2CO), 29.1–28.7 (8C), 26.6 (2× CH_2CH_2CO), 24.6 (CH_2CH_2CHBr) ppm. MS/CI (isobutene): *m*/*z* (%): 745 $[MH]^+$.

2.7 1,3-(10,11-Dibromoundecanoyl)-2-(10-undecenoyl)triglyceride 6

1,3-(10,11 Dibromoundecanoyl)diglyceride **9** (4.2g, 5.6 mmol) in 21 mL of pyridine were cooled to 0°C. After addition of 10-undecenoyl chloride (2.86 g, 14.11 mmol) the reaction mixture was heated for 1 h at 65°C and then poured into 250 mL of ice water and acidified with conc. HCl. The sample was extracted with petroleum ether (800 mL) and the organic phase was washed with sodium bicarbonate (3 mL × 200 mL), dried over Na_2SO_4, filtrated, and the solvent was removed *in vacuo*. Column chromatography of the residue (5.74 g) was performed using silica gel 60 and petroleum ether/diethyl ether (7:3) as eluent to give product **6** in a yield of 3.96 g (77.7%).

^{1}H NMR (500.1 MHz, $CDCl_3$): $\delta = 5.82$ (ddt, $J = 17.2$, 10.4, 6.8 Hz, 1H, $CH{=}CH_2$), 5.26 (m, 1H, CHO), 4.99 (ddt, $J = 17.2$, 3.9, 1.7 Hz, 1H, $CH{=}CH_a$), 4.93 (ddt, $J = 10.4$, 3.9, 1.2 Hz, 1H, $CH{=}CH_b$), 4.29 (m, 2H, 2× CHBr), 4.16 (m, 4H, 2× CH_2O), 3.88 (dd, $J = 10.5$, 4.7 Hz, 2H, 2× $CH_{a,b}Br$), 3.63 (dd, $J = 10.5$, 10.5 Hz, 2H, 2× $CH_{a,b}Br$), 2.31 (t, $J = 7.5$ Hz, 6H, 3 × CH_2CO), 2.13 (m, 2H, 2× $CHBrCH_{a,b}$), 2.04 (dt, $J = 3.9$, 7.8 Hz, 2H, $CH_2CH{=}CH_2$), 1.79 (m, 2H, 2× $CHBrCH_{a,b}$), 1.63 (m, 8H, $COCH_2CH_2$), 1.30 (m, CH_2). ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta = 173.1$ (2× CO), 172.7 (CO), 139.1 ($CH{=}CH_2$), 114.14 ($CH{=}CH_2$), 68.9 (OCH), 62.1 (2× OCH_2), 53.0 (2× CHBr), 36.3 and 36.0 (2× CH_2Br and 2× CH_2CHBr), 34.2–33.7 (CH_2), 29.3–28.7 (CH_2), 26.6 (2× CH_2CH_2CO), 24.8 ($COCH_2$ CH_2), 24.6 (2× CH_2CH_2CHBr) ppm. MS/CI (isobutene): *m*/*z* (%): 911 $[MH]^+$.

2.8 Brominated di-triglyceride 10

Compound **6** (180 mg, 0.2 mmol) and second generation Grubbs catalyst (G-II, 4.5 mg, 0.0053 mmol) were stirred under nitrogen atmosphere some minutes. Then the reaction was continued *in vacuo* (20 mbar) at 40°C. After 24 h the reaction was stopped by addition of ethyl vinyl ether. *n*-Hexane (10 mL), diethyl ether (10 mL), and silica gel (1 g) were added and the sample was stirred for 1 h. After filtration the solvent was evaporated and the residue was dried *in vacuo*. Yield: 0.12 g (67%).

^{1}H NMR (500.1 MHz, $CDCl_3$): $\delta = 5.31$ (m, 2H, CH=CH), 5.25 (m, 2H, 2× CHO), 4.23 (m, 4H, 4× CHBr), 4.08 (m, 8H, 4× CH_2O), 3.78 (dd, $J = 10.5$, 4.7 Hz, 4H, 4× $CH_{a,b}Br$), 3.56 (dd, $J = 10.5$, 10.5 Hz, 4H, 4× $CH_{a,b}Br$), 2.25 (t, $J = 7.9$ Hz, 12H, 6× CH_2CO), 2.07 (m, 4H, 4× $CHBrCH_{a,b}$), 1.89 (m, 4H, 2× $CH_2CH{=}CH$), 1.72 (m, 4H, 4× $CHBrCH_{a,b}$), 1.55 (m, 12H, 6× $COCH_2CH_2$), 1.30–1.16 (m, 60H, CH_2). ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta = 173.7$ (4× CO), 173.2 (2× CO), 130.7 (C=C), 69.3 (2× OCH), 62.5 (4× OCH_2), 54.0, 53.5 (4× CHBr), 36.8 and 36.4 (4× CH_2Br and 4× CH_2CHBr), 34.6 (2× CH_2CO), 34.4 (4× CH_2CO), 33.0 (2× $CH_2CH{=}CH$), 29.8–29.2 (CH_2), 27.1 (4× CH_2CH_2CHBr), 25.2 (6× CH_2CH_2CO) ppm.

2.9 Compound 5

Brominated di-triglyceride **10** (120 mg, 6.7 mmol) dissolved in dichloromethane (25 mL) was hydrogenated using Pd/C

(10% Pd) as catalyst. After filtration and evaporation of the solvent product **5** was obtained in 75% yield (90 mg).

^{1}H NMR (500.1 MHz, $CDCl_3$): $\delta = 5.25$ (m, 2H, 2× CHO), 4.23 (m, 4H, 4× CHBr), 4.09 (m, 8H, 4× CH_2O), 3.78 (dd, $\mathcal{J} = 10.6$, 4.8 Hz, 4H, 4× $CH_{a,b}Br$), 3.56 (dd, $\mathcal{J} = 10.3$, 10.3 Hz, 4H, 4× $CH_{a,b}Br$), 2.25 (t, $\mathcal{J} = 8.0$ Hz, 12H, 6× CH_2CO), 2.06 (m, 4H, 4× $CHBrCH_{a,b}$), 1.72 (m, 4H, 4× $CHBrCH_{a,b}$), 1.56 (m, 12H, 6× $COCH_2CH_2$), 1.35–1.15 (CH_2).

^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta = 173.2$ (4× CO), 172.8 (2× CO), 68.8 (2× OCH), 62.0 (4× OCH_2), 53.5, 53.0 (4× CHBr), 36.3 and 35.9 (4× CH_2Br and 4× CH_2CHBr), 34.2 (2× CH_2CO), 34.1 (4× CH_2CO), 29.6–28.7 (CH_2), 26.6 (4× CH_2CH_2CHBr), 24.8 (6× CH_2CH_2CO) ppm.

2.10 Compound 4

Debromination of compound **5** was carried out by heating of **5** (180 mg, 0.1 mmol) with zinc (65.4 mg, 1 mmol) in methanol abs. (10 mL) under reflux for 30 min. Then the solvent was evaporated *in vacuo* and the residue was dissolved in dichloromethane (60 mL). After filtration the organic layer was washed with H_2O (2 mL × 30 mL), dried with Na_2SO_4, filtrated, and the solvent was evaporated *in vacuo*. Yield: 0.11 g (95.3%).

^{1}H NMR (500.1 MHz, $CDCl_3$): $\delta = 5.74$ (ddt, $\mathcal{J} = 17.1$, 10.5, 6.8 Hz, 4H, $CH=CH_2$), 5.21 (m, 2H, CHO), 4.89 (dd, $\mathcal{J} = 17.1$, 10.6 Hz, 8H, $CH=CH_{a,b}$), 4.23 (dd, $\mathcal{J} = 12.2$, 4.6 Hz, 4H, $CH_{a,b}O$), 4.08 (dd, $\mathcal{J} = 12.2$, 6.2 Hz, 4H, $CH_{a,b}O$), 2.24 (t, $\mathcal{J} = 8.0$ Hz, 12H, CH_2CO), 1.98 (dt, $\mathcal{J} = 6.8$, 8.0 Hz, 8H, $CH_2CH=CH_2$), 1.55 (m, 12H, $COCH_2CH_2$), 1.27 (m, 68 H, CH_2).

^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta = 173.2$ (4× CO), 172.8 (2× CO), 139.0 ($CH=CH_2$), 114.1 ($CH=CH_2$), 68.8 (2× OCH), 62.0 (4× OCH_2), 34.2–33.7 (10C, CH_2CO and $CH_2CH=CH_2$), 24.8 (6× CH_2CH_2CO) ppm. MS/CI (isobutane): *m*/*z* (%): 1157 $[MH]^+$ (100), side products: 1143$[MH]^+$ (58), 1129 $[MH]^+$ (18), and 1171$[MH]^+$ (4).

2.11 Cross-metathesis product 3

A mixture of compound **4** (110 mg, 0.1 mmol) and MA (328 mg, 3.8 mmol) in a round bottomed flask was degassed and then flushed with nitrogen (two freeze-thaw cycles). After addition of HG-II (2.5 mg, 0.004 mmol), the sample was heated under a nitrogen atmosphere to 60°C and stirred for 24 h. Then the reaction was stopped by addition of ethyl vinyl ether and the sample was subjected to Kugelrohr distillation (70°C, 4×10^{-3} mbar). Excess of ethyl vinyl ether was removed by "Kugelrohr distillation" and the residue was purified by filtration over silica gel (petroleum ether/diethyl ether = 1:1). The solvent was evaporated *in vacuo*. Yield: 0.70 g (51%).

^{1}H NMR (500.1 MHz, $CDCl_3$): $\delta = 6.89$ (dt, $\mathcal{J} = 16.0$, 7.5 Hz, 4H, $CH=CHCO$), 5.72 (d, $\mathcal{J} = 16.0$ Hz, 4H, $CH=CHCO$), 5.21 (m, 2H, CHO), 4.23 (dd, $\mathcal{J} = 12.5$, 4.8 Hz, 4H, CH_2O), 4.08 (dd, $\mathcal{J} = 12.5$, 6.3 Hz, 4H, CH_2O), 3.65 (s, 12 H, OCH_3), 2.25 (t, $\mathcal{J} = 8.0$ Hz, 4H, CH_2CO), 2.24 (t, $\mathcal{J} = 8.0$ Hz, 8H, CH_2CO), 2.12 (dt, $\mathcal{J} = 8.2$, 7.5 Hz, 8H, $CH_2CH=CH$), 1.55 (m, 12H, $COCH_2CH_2$), 1.40 (m, 8H, CH_2), 1.20 (m, CH_2). ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta = 173.1$ (4× CO), 172.7 (2× CO), 167.0 (4× CO), 149.5 ($COCH=CH$), 120.8 ($COCH=CH$), 68.1 (2× OCH), 62.0 (4× OCH_2), 51.2 (OCH_3), 34.0 (6× CH_2CO), 32.0 (4× $CH_2CH=CH_2$), 29.6–28.6 (CH_2), 27.9, 24.8 (6× CH_2CH_2CO) ppm. MS (ESI-positive): $m/z = 1394$ ($[M\,Li]^+$).

3 Results and discussion

Studying the ATMET reaction of glyceryl triundecenoate **1** with MA as chain stopper our interest was focused to the products of lower molecular weight, which were formed in the first steps of ATMET in varying amounts depending on the ratio of MA and triglyceride, reaction time, and temperature [6]. The ATMET reaction of **1** was performed with three equivalents of MA in the presence of HG-II. After a reaction time of 5 h at 75°C we could isolate, besides branched macromolecules (Fig. 1), the main products, dimer **2** (Fig. 2) and compounds **11** and **12** (Fig. 4), respectively,

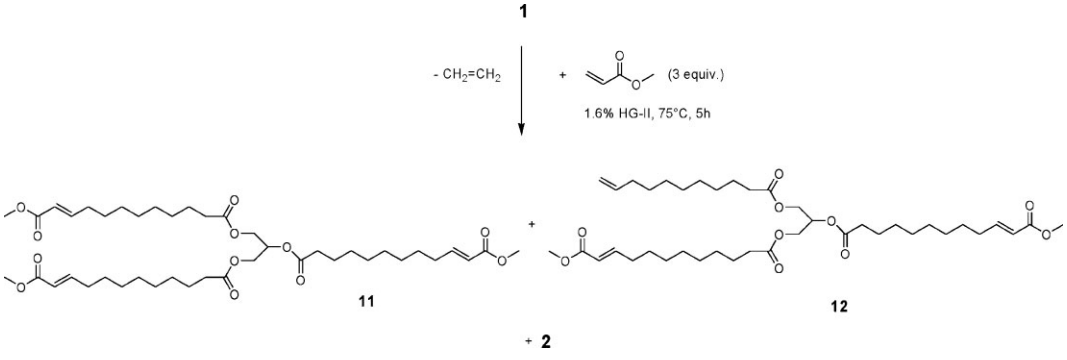

Figure 4. ATMET reaction of glyceryl triundec-10-enoate **1** with MA to give in the first step products with low molecular weight such as **11**, **12**, and dimer **2**.

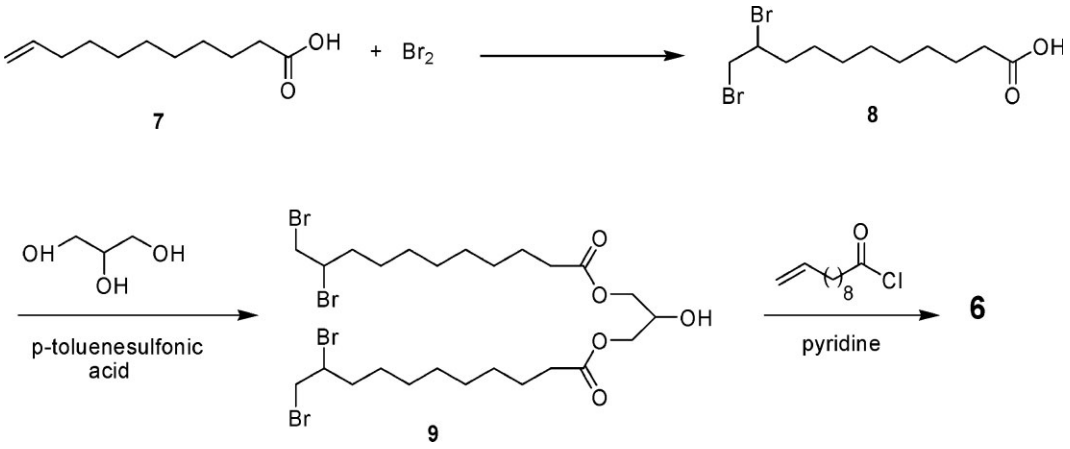

Figure 5. Synthesis of *tetra*-bromo triglyceride **6** *via* 10,11-dibromo undecanoic acid **8** and 1,3-diglyceride **9**.

by column chromatography (ratio of **11**:**12**:**2** = 7:1:1). The formation of **2**, which was clearly identified by ESI-MS and NMR-spectroscopy, can be rationalized by self-metathesis of cross-metathesis product **11**.

The highly functionalized dimer **2** or alternatively, compound **3** (Fig. 2) should be of interest as starting material for a number of follow-up reactions and it seemed to be worth to develop a reaction sequence for an independent synthesis. Initially, our interest was focused to the synthesis of compound **6**, which was required as substrate for the self-metathesis reaction on the way to the preparation of the desired molecule **3**. In the first step of the reaction sequence 10-undecenoic acid **7** was brominated to give in quantitative yield 10,11-dibromo undecanoic acid **8**. (Fig. 5) Full conversion of the C,C-double bond was indicated by the respective ^{13}C and ^{1}H NMR spectra showing no signals neither for olefinic carbon atoms nor protons. Recrystallization of product **8** was not necessary due to its high purity. The brominated fatty acid **8** was esterified with glycerol using a ratio of **8** and glycerol of 2.5:1 in the presence of *p*-toluene sulfonic acid. The crude product contained besides the desired 1,3-diglyceride **9** which was formed as main product the respective 1,2-di-, mono-, and triglycerides as minor compounds. Separation and purification of compound **9** was achieved by column chromatography. The position of the hydroxyl group of **9** at C2 of the glycerol skeleton was confirmed by the ^{13}C NMR data showing the respective signal at 68.3 ppm. The preparation of *tetra*-bromo triglyceride **6** was carried out by alcoholysis of 10-undecenoic acid chloride with 1,3-diglyceride **9**.

After purification by column chromatography compound **6** was characterized by NMR showing the respective signals for the terminal C,C-double bond at 139.1 and 114.1 ppm in the ^{13}C NMR spectrum and at 5.82 ppm (CH=CH_2), 4.99 ppm (CH=CH_a), and 4.93 ppm (CH=CH_b) in the ^{1}H NMR spectrum. Having the unsaturated *tetra*-bromo

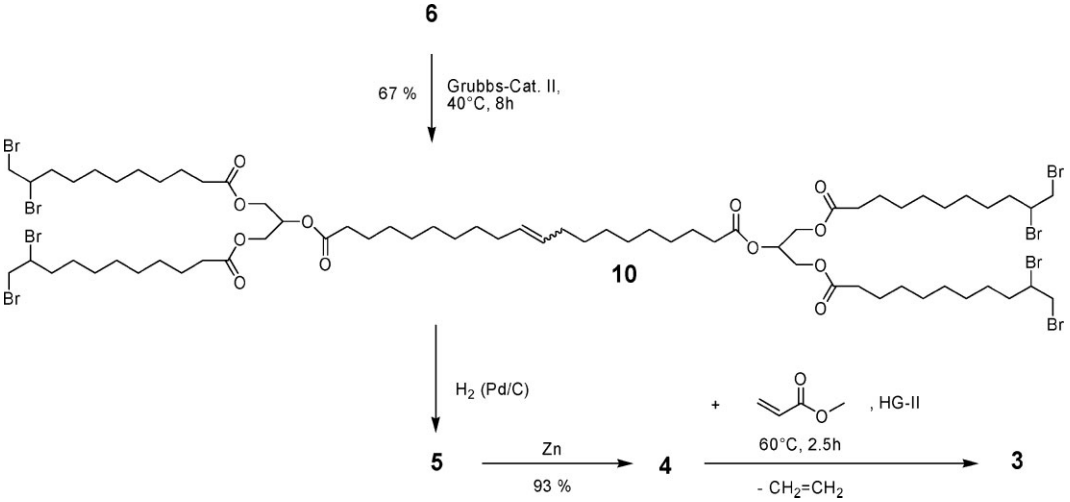

Figure 6. Self-metathesis of *tetra*-bromo triglyceride **6** followed by hydrogenation and debromination of the resulting *tetra*-bromo di-triglyceride **10** to give di-triglyceride **4** with four terminal C,C-double-bonds. Cross-metathesis of **4** with MA yielded di-trigyceride **3**.

triglyceride **6** in hands the self-metathesis reaction could be carried out using **6** as starting material. The reaction was performed with the second generation Grubbs-catalyst, which shows high activity under mild reaction conditions for metathesis reactions of triglycerides [7]. Using an amount of 1.4 mol% of the catalyst full conversion of compound **6** was achieved after a reaction time of 8 h at 40°C to give dimer **10** (Fig. 6). Signals indicating a terminal C,C-double bond could not be detected neither in the ^{13}C nor in the ^{1}H NMR spectrum. The self-metathesis of **6** proceeded by formation of a new, internal C,C-double bond.

Quantitative hydrogenation of the internal double bond of dimer **10** followed by debromination with zinc gave di-triglyceride **4** with four terminal C,C-double bonds. The CI mass spectrum of **4** showed besides the expected signal of $m/z = 1157$ $[MH]^+$ further signals at $m/z = 1143[MH]^+$, 1129 $[MH]^+$, and 1171 $[MH]^+$ (differences of 14 Da, methylene units) because of isomerization side-reactions of the C,C-double bond during self-metathesis reaction of **6** to give **10**. Such isomerizations caused by the intermediate formation of Ruthenium-hydride species giving rise to shorter as well as longer chain metathesis products are well known [8]. Tetraen **4** should be an interesting monomer not only for metathesis reactions, but also for thiol-ene additions and in general as a building block for branched polymers as well as dendrimers.

The cross-metathesis reaction of **4** with MA, which was used in a large excess to suppress the ATMET polymerization was carried out in the presence of Hoveyda–Grubbs second generation metathesis catalyst (HG-II), which is known to be very efficient in cross-metathesis reactions of electron poor double bonds and MA [9]. After a reaction time of 2.5 h at 50°C the highly functionalized dimer **3** was obtained in 51% yield. All the double bonds included in **4** reacted with MA. The structure of product **3** was unambiguously confirmed by NMR showing the signals for α,β-unsaturated methyl ester functionality at 6.89 and 5.72 ppm in the ^{1}H and 149.5 and 120.8 ppm in the ^{13}C NMR spectrum. The C,C-double bonds were *E*-configured as indicated by the coupling constants ($\mathcal{J} = 16.0$ Hz) of the olefinic protons. Furthermore, from the ratio (1:1) of the integrals of the methyl groups (OCH_3, 12H) and the methylene groups in α-position to the carbonyl groups (CH_2COO, 12H) in the ^{1}H NMR spectrum it can be concluded that neither oligomers nor polymers were formed in this cross-metathesis reaction. ^{1}H and ^{13}C NMR spectra of products **2** and **3** are essentially identical with the difference of the signals of the internal C,C-double bond present in compound **3**. The ESI/MS spectrum of **3** showed the expected lithiated molecular ion of $m/z = 1394$ $[M\,Li]^+$. In contrast, compound **2** having two hydrogen atoms less showed a sodiated molecular ion of $m/z = 1408$ ($[M\,Na]^+$).

4 Conclusions

In the first steps of the ATMET reaction of unsaturated triglycerides and MA as chain stopper highly functionalized dimeric compounds are formed. The isolation and unambiguous characterization of these products was shown and furthermore the independent synthesis including a seven step reaction sequence to give compared to the ATMET reaction, exclusively the desired partially hydrogenated cross- and self-metathesis dimer. The described reaction sequence is allows to build up high molecular dendrimers in few reaction steps using as starting material triglyceride **6** which can easily be synthesized in high amounts.

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