

Fatty acid derived monomers and related polymers via thiol-ene (click) additions

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Experimental Section

Materials. 10-undecenoic acid (Aldrich, 98%), 10-undecen-1-ol (Aldrich, 98%), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD, Aldrich, 98%), 1-thioglycerol (Aldrich, >99%), 1,4-butanedithiol (Aldrich, >97%), 2-mercaptoethanol (Aldrich, >99%), methyl thioglycolate (Aldrich, >97%), tetradecane (Aldrich, ≥99,5%), ethylene glycol (Aldrich, >99%), 1,3-propanediol (Aldrich, >99%), glycerol (Aldrich, >99%), and 2,2-dimethoxy-2-phenylacetophenone (DMPA, Aldrich, 99%) were used as received. 2,2'-Azobis(2-methylpropionitrile) (AIBN, Aldrich, 98%) was used after recrystallization from methanol.

Methyl 10-undecenoate (**2**) was prepared by esterification with methanol from corresponding 10-undecenoic acid according to a standard laboratory procedure.

General Methods.

Thin layer chromatography (TLC) was performed on silica gel TLC-cards (layer thickness 0.20 mm, Fluka). Compounds were visualized by permanganate reagent. For column chromatography silica gel 60 (0.035-0.070 mm, Fluka) was used.

¹H-NMR spectra were recorded in CDCl₃ on Bruker AVANCE DPX spectrometers operating at 300 and 500 MHz. Chemical shifts (δ) are reported in parts per million relative to the internal standard tetramethylsilane (TMS, δ = 0.00 ppm). For the analyses of the polymers the relaxation time was set to 5 seconds.

Mass spectra (ESI) were recorded on a VARIAN 500-MS ion trap mass spectrometer with the TurboDDSTM option installed. Samples were introduced by direct infusion with a syringe pump. Nitrogen served both as the nebulizer gas and the drying gas. Helium served as cooling gas for the ion trap and collision gas for MSn. Nitrogen was generated by a nitrogen generator Nitrox from Dominick Hunter.

GC-MS (EI) chromatograms were recorded using two instruments: 1) A VARIAN 3900 GC instrument with a capillary column FactorFourTM VF- 5ms (30 m × 0.25 mm × 0.25 μm) and a Saturn 2100T ion trap mass

detector. Scans were performed from 40 to 650 m/z at rate of $1.0 \text{ scans} \times \text{s}^{-1}$. The oven temperature program was: initial temperature $95 \text{ }^\circ\text{C}$, hold for 1 min, ramp at $15 \text{ }^\circ\text{C} \times \text{min}^{-1}$ to $200 \text{ }^\circ\text{C}$, hold for 2 min, ramp at $15 \text{ }^\circ\text{C} \times \text{min}^{-1}$ to $325 \text{ }^\circ\text{C}$, hold for 5 min. The injector transfer line temperature was set to $250 \text{ }^\circ\text{C}$. Measurements were performed in the split-split mode (split ratio 50:1) using helium as carrier gas (flow rate $1.0 \text{ mL} \times \text{min}^{-1}$).

2) A HP 5890 Series II instrument with a capillary column ($30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \text{ }\mu\text{m}$) and a HP 5971A Mass Selective Detector. The oven temperature program was: initial temperature $70 \text{ }^\circ\text{C}$, ramp at $25 \text{ }^\circ\text{C} \times \text{min}^{-1}$ to $280 \text{ }^\circ\text{C}$, hold for 5 min. The injector temperature was set to $250 \text{ }^\circ\text{C}$. Measurements were performed in the split-split mode (split ratio 1:1) using He as carrier gas (flow rate $0.8 \text{ mL} \times \text{min}^{-1}$).

Polymer molecular weights were determined using an SEC System LC-20 A from Shimadzu equipped with a SIL-20A auto sampler, three PSS SDV columns ($5 \text{ }\mu\text{m}$, $300 \text{ mm} \times 7.5 \text{ mm}$, 100 \AA , 1000 \AA , 10000 \AA), and a RID-10A refractive index detector in THF (flow rate $1 \text{ mL} \times \text{min}^{-1}$) at $50 \text{ }^\circ\text{C}$. All determinations of molar mass were performed relative to PMMA standards (Polymer Standards Service, M_p 1100–981.000 Da).

Differential scanning calorimetry (DSC) experiments were carried out under a nitrogen atmosphere at a heating rate of 10, 5, and $20 \text{ }^\circ\text{C} \times \text{min}^{-1}$ (see results and discussion part) with a DSC821e (Mettler Toledo) calorimeter up to a temperature of $150 \text{ }^\circ\text{C}$ using a sample mass of approximately 4 mg. The melting temperature, T_m , was recorded as the peak of the endotherm on the second heating scan unless annealing was used as a pretreatment.

Thermogravimetric analysis (TGA) was performed on a TGA/SDTA851e instrument (Mettler Toledo) at a heating rate of $10 \text{ }^\circ\text{C} \times \text{min}^{-1}$ under nitrogen. The weights of the samples were about of 8 mg.

Monomer Synthesis

Optimization reactions were carried out with a Radleys Carousel 12 plus reactor system using of ($500 \mu\text{L}$, 2.17 mmol) methyl 10-undecenoate **2** and tetradecane ($10 \text{ mol}\%$ of **1**) as internal standard for GC analysis.

Methyl 11-((2,3-dihydroxypropyl)thio)undecanoate (M1): **2** (9.915 g , 50 mmol) and 1-thioglycerol (5.408 g , 50 mmol) were weighed into a flask and vacuum was subsequently applied for 5 minutes for degassing. The closed flask was then stirred at $35 \text{ }^\circ\text{C}$ and 1500 rpm for 6 days. Excess methyl undecenoate was then removed via distillation under reduced pressure and the residue was precipitated into hexane (10.37 g , 66%).

$^1\text{H NMR}$ (500 MHz , CDCl_3 , δ): 3.72 (m, 1H, HO-CH<), 3.69 (dd, $J = 3.05$ and 11.60 Hz , 1H, HO-CH_a(H_b)-), 3.59 (s, 3H, CH₃-OOC-), 3.49 (dd, $J = 5.76$ and 11.14 Hz , 1H, HO-CH_a(H_b)-), 2.63 (dd, $J = 4.32$ and 13.69 Hz , 1H, -CH_c(H_d)-S-), 2.52 (dd, $J = 8.38$ and 13.63 Hz , 1H, -CH_c(H_d)-S-), 2.46 (t, $J = 7.42 \text{ Hz}$, 2H, -S-CH₂-), 2.23 (t, $J = 7.54 \text{ Hz}$, 2H, -CH₂-COO-), 1.55 - 1.45 (m, 4H, -SCH₂-CH₂- and -CH₂-CH₂COO-), 1.35 - 1.15 (m, aliphatic, -[CH₂]-) ppm. $^{13}\text{C NMR}$ (300 MHz , CDCl_3 , δ): 174.8 (C=O ester), 70.68 (HO-CH< secondary alcohol), 65.74 (HO-CH₂- primary alcohol), 51.84 (H₃C-O- ester), 36.00 (-S-CH₂-), 34.46 (-C=O-CH₂-), 32.83 (-CH₂-S-), 29.55 (-CH₂- aliphatic), 25.28 (-CH₂- aliphatic) ppm. MS (ESI-positive, MeOH): $m/z = 329.1$ ([M+Na]⁺, calc. 329.2)

Methyl 11-((2-hydroxyethyl)thio)undecanoate (M2): **2** (3.968 g, 20 mmol) and mercaptoethanol (1.586 g, 20 mmol) were weighed into a flask and vacuum was subsequently applied for 5 minutes for degassing. Capped vessels were left to stir at 35 °C and 1500 rpm for 68 hours. A white solid product was isolated by column chromatography (hexane:ethyl acetate = 1:1) (5.21 g, 93%). ¹H NMR (500 MHz, CDCl₃, δ): 3.71 (t, *J* = 5.97 Hz, 2H, HO-CH₂-), 3.66 (s, 3H, CH₃-OOC-), 2.73 (t, *J* = 5.99 Hz, 2H, HOCH₂-CH₂-S-), 2.51 (t, *J* = 7.32 Hz, 2H, -S-CH₂-CH₂), 2.26 (t, *J* = 7.56 Hz, 2H, -CH₂-COO-), 1.56 (m, 4H, -SCH₂-CH₂- and -CH₂-CH₂COO-), 1.35-1.15 (m, aliphatic, -[CH₂]-) ppm. ¹³C NMR (300 MHz, CDCl₃, δ): 174.70 (C=O ester), 60.73 (HO-CH₂ alcohol), 51.80 (H₃C-O- ester), 35.60 (-S-CH₂-), 34.46 (-C=O-CH₂-), 32.08 (-CH₂-S-), 29.52 (-CH₂- aliphatic), 25.29 (-CH₂- aliphatic) ppm. MS (ESI-positive, MeOH): *m/z* = 329.1 ([M+Na]⁺, calc. 329.2) MS (ESI-positive, MeOH): *m/z* = 299.1 ([M+Na]⁺, calc. 299.2)

Methyl 11-((2-methoxy-2-oxoethyl)thio)undecanoate (M3): **2** (3.97g, 20 mmol) and methyl thioglycolate (2.12g, 20 mmol) were weighed into a flask and stirred without degassing at room temperature at 1500 rpm for 48 hours. The conversion of the reaction and the purity of the obtained white solid was >99%, thus no further purification of the obtained white solid was carried out. ¹H NMR (500 MHz, CDCl₃, δ): 3.71 (s, 3H, CH₃-OCOCH₂CH₂-), 3.64 (s, 3H, CH₃-OCOCH₂S-), 3.20 (s, 2H, -OCO-CH₂-S-), 2.59 (t, *J* = 7.40 Hz, 2H, -CH₂S-CH₂-), 2.27 (t, *J* = 7.55 Hz, 2H, -OCO-CH₂-), 1.61 - 1.53 (m, 4H, -SCH₂-CH₂- and -CH₂-CH₂COO-), 1.36-1.22 (m, aliphatic, -[CH₂]-) ppm. ¹³C NMR (300 MHz, CDCl₃, δ): 174.60 (C=O ester), 171.38 (-SCH₂-C=O-), 52.66 (H₃C-OCOCH₂S- ester), 34.44 (-S-CH₂-C=O-), 33.84 (-C=O-CH₂-), 33.09 (-CH₂-S-), 29.47 (-CH₂- aliphatic), 25.29 (-CH₂- aliphatic) ppm. MS (ESI-positive, MeOH): *m/z* = 327.1 ([M+Na]⁺, calc. 327.2)

Dimethyl 11,11'-(butane-1,4-diylbis(sulfanediyl))diundecanoate (M4): 3.97g **1** (20 mmol) and 1.23 g 1,4-butanedithiol (10 mmol) were weighed into flask, degassed, and stirred at 60 °C and 1500 rpm. After 5 hours, the reaction mixture solidified. The mixture was collected in dichloromethane and precipitated into hexane (3.82 g, 73.5%). ¹H NMR (500 MHz, CDCl₃, δ): 3.66 (s, 3H, H₃C- OOC-), 2.51 (t, *J* = 7.41 Hz, 8H, 2x-CH₂-S-CH₂-), 2.30 (t, *J* = 7.56 Hz, 4H, -CH₂-COO-), 1.71-1.65 (m, 4H, -SCH₂-[CH₂]₂-CH₂S-), 1.62-1.51 (m, 8H, 2x-SCH₂-CH₂- and 2x-OCCH₂-CH₂-), 1.25-1.12 (m, aliphatic, 2x-[CH₂]-) ppm. ¹³C NMR (300 MHz, CDCl₃, δ): 174.65 (C=O ester), 51.80 (H₃C-O- ester), 34.48 (-C=O-CH₂-), 32.54 (-CH₂-S-), 32.10 (-SCH₂-CH₂-), 29.61 (-CH₂- aliphatic), 25.33 (-CH₂- aliphatic) ppm. MS (ESI-positive, MeOH): *m/z* = 541.2 ([M+Na]⁺, calc. 541.3)

11,11'-(butane-1,4-diylbis(sulfanediyl))bis(undecan-1-ol) (M5): 10-Undecen-1-ol (3.406 g, 20 mmol) and 1,4-butanedithiol (1.222 g, 10 mmol) were weighed into flask, degassed, and stirred at 70 °C and 1500 rpm. After 3 days, the reaction mixture was completely solidified. The product was purified by recrystallization

from MeOH (3.80 g, 82.1%). ^1H NMR (300 MHz, CDCl_3 , δ): 3.56 (t, $J = 6.60$ Hz, 4H, HO- CH_2 -), 2.51 (t, $J = 7.43$ Hz, 8H, 2x- CH_2 -S- CH_2 -), 1.78-1.66 (m, 4H, - SCH_2 -[CH_2] $_2$ - CH_2 S-), 1.64-1.20 (m, aliphatic, 2x-[CH_2]-) ppm. MS (ESI-positive, MeOH): $m/z = 485.3$ ($[\text{M}+\text{Na}]^+$, calc. 485.4)

Polymerization Reactions

All polycondensation reactions were carried out at 120 °C applying continuous vacuum (200±35 mbar) in order to remove the released methanol. 5 mol% of TBD was used as catalyst per mol of ester groups present in the respective monomers.

P1: 0.5181 g (1.69 mmol) of **M1** and 6.17 μL (0.08 mmol) of glycerol were polymerized with 0.0118 g (0.08 mmol) of TBD for 8h. The polymer was purified by precipitation from THF into hexane (0.3061 g, 66%). ^1H NMR (300 MHz, CDCl_3 , δ): 5.19-5.08 (-COO CH_2 (CH -OOC) CH_2 -S), 5.02-4.92 (HO CH_2 (CH -OOC) CH_2 -S-), 4.36 (-COO CH_aH_b (CH -OOC) CH_2 -S-), 4.25-4.05 (-COO CH_aH_b (CH -OOC) CH_2 -S- and - $\text{SCH}_2\text{CH}(\text{OH})$ - $\text{CH}_a(\text{H}_b)$ -OOC-), 4.00-3.88 (- SCH_2 - $\text{CH}(\text{OH})$ - CH_2 OOC-), 3.58 (- $\text{SCH}_2\text{CH}(\text{OH})$ - $\text{CH}_a(\text{H}_b)$ -OOC-), 2.78-2.57 (> CH - CH_2 -S-), 2.55 (-[CH_2] $_8$ - CH_2 -S-), 2.36 (-OOC- CH_2 -), 1.72-1.14 (m, aliphatic) ppm.

P2: 0.5012 g (1.81 mmol) of **M2** was polymerized with 0.0117 g (0.08 mmol) of TBD for 8h. The polymer was purified via precipitation from THF into hexane (0.3756 g, 85%). ^1H NMR (300 MHz, CDCl_3 , δ): 4.22 (-COO- CH_2 -), 3.73 (H_3CO -CO-), 3.68 (HO- CH_2 -), 2.74 (-O CH_2 - CH_2 -S-), 2.56 (- CH_2 -S- CH_2 -), 2.32 (- CH_2 -COO-), 1.68-1.53 (-OOC CH_2 - CH_2 - and - CH_2 - CH_2 -S-), 1.42-1.22 (m, aliphatic) ppm.

P35: 0.3813 g (1.25 mmol) of **M3** and 0.5799 g (1.25 mmol) of **M5** were polymerized with 0.0174 g (0.12 mmol) of TBD for 8h. The polymer was purified via precipitation from THF into methanol (0.7598 g, 86%). ^1H NMR (300 MHz, CDCl_3 , δ): 4.12 (- SCH_2COO - CH_2 -), 4.05 (- $\text{CH}_2\text{CH}_2\text{COO}$ - CH_2 -), 3.21 (- SCH_2COO -), 2.63 (- CH_2 - CH_2 - SCH_2COO -), 2.50 (- CH_2 -S- CH_2 -), 2.29 (-OOC- CH_2 -), 1.73-1.18 (m, aliphatic) ppm.

P45: 0.3328 g (0.64 mmol) of **M4** and 0.2968 g (0.64 mmol) of **M5** were polymerized using 0.0091 g (0.06 mmol) of TBD for 8h. The polymer was purified via precipitation from THF into methanol (0.4081 g, 69%). ^1H NMR (300 MHz, CDCl_3 , δ): 4.05 (-COO- CH_2 -), 2.54 (- CH_2 -S- CH_2 -), 2.28 (-OOC- CH_2 -), 1.76-1.71 (- SCH_2 -[CH_2] $_2$ - CH_2 S-), 1.68-1.57 (m, aliphatic) ppm.

Additional Figures

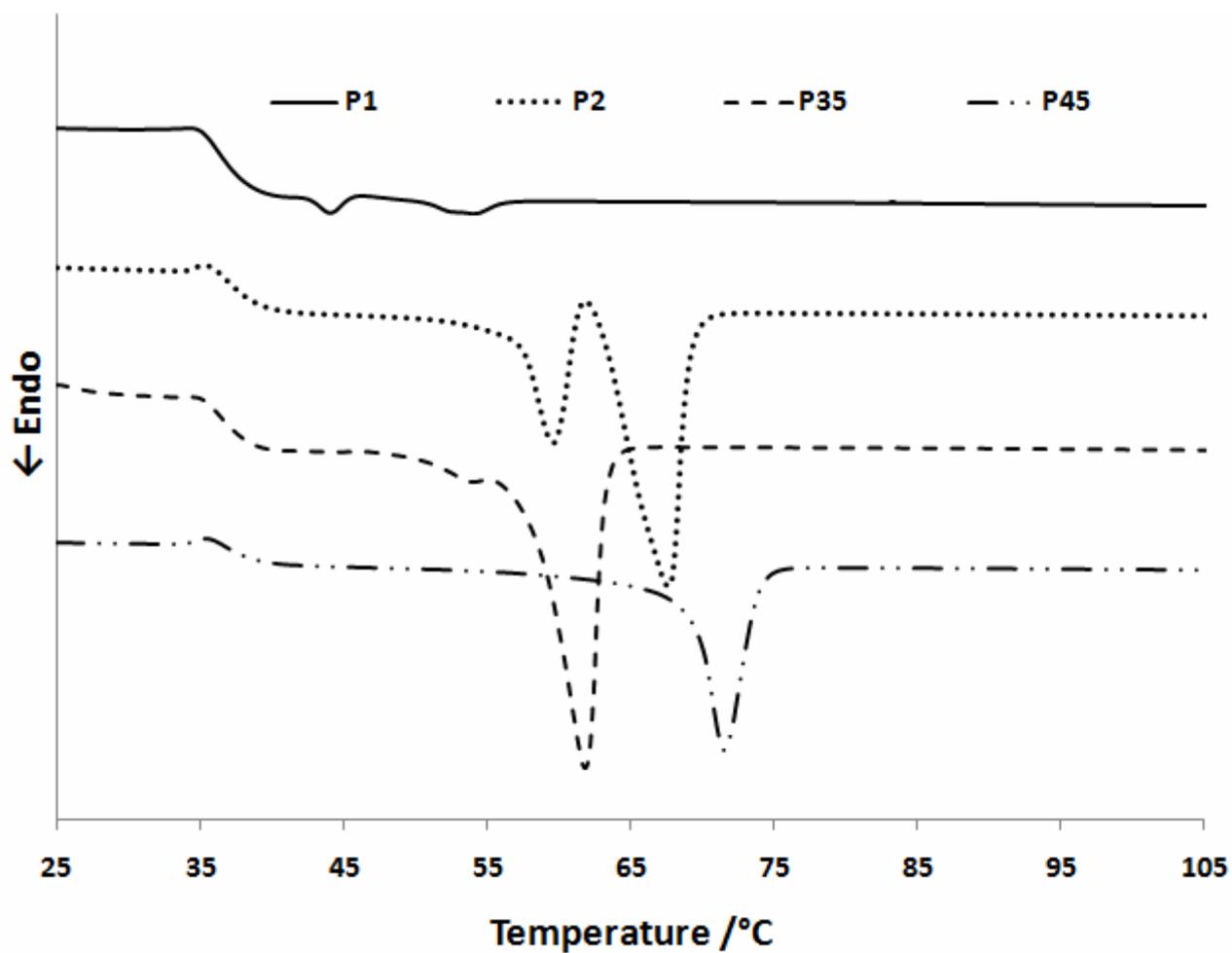


Figure S1: DSC thermogram of P1, P2, P35, and P45 (2nd run) with 10 °C/min heating rate.