Supporting Information

The unrevealed potential of elemental sulfur for the synthesis of high sulfur content bio-based aliphatic polyesters

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A. Experimental procedures

A.1 Materials

Unless otherwise stated all chemicals were used as received. Oleic acid (Merck, technical grade), sulfuric acid (H_2SO_4, VWR, AnalaR NORMAPUR), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD, VWR, ≥98%), 1,6-hexanediol (Sigma Aldrich, 99 %), hydroquinone (VWR, 99 %), thioacetic acid (Acros Organics, 98 %), iodine (I_2, Acros, 99%), elemental sulfur (S_8, Sigma, powder for external use Ph Eur, BP), magnesium sulfate ($MgSO_4$, Roth, ≥99 %), dichloromethane (DCM, VWR, AnalaR NORMAPUR), methanol (MeOH, VWR, AnalaR NORMAPUR), methanol (MeOH, Acros, 99.9 %, extra dry), diethyl ether (Et_2O, Acros Organics, ACS reagent, anhydrous), aluminium oxide 90 active basic (Al_2O_3, Millipore, 0.063-0.200 mm), sodium sulfite (Na_2SO_3 Merck, ≥98 %)), sodium hydroxide (NaOH, Merck).

Methyl oleate (**MO**) was synthesized from oleic acid according to a modified procedure from the literature.[1]

A.2. Synthesis of M1

A.2.1 Synthesis of methyl 9(10)-(acetylthio)stearate

According to a modified procedure from the literature,[2] 20.25 g of methyl oleate (68.0 mmol, 1.0 eq.) and 15.6 g of thioacetic acid (205 mmol, 14.4 mL, 3.0 eq.) were added to a round bottom flask under inert gas. The respective reaction mixture was irradiated with Arimed B6 lamp (approx. 300 - 400 nm, max. approx. 330 - 350 nm) in a distance of 5 cm inside a custom-built photoreactor for 26 hours at ambient temperature under inert atmosphere. After the reaction had been completed, the excess of thioacetic acid was carefully removed under reduced pressure. The crude product was purified by column chromatography on silica (hexane/ethyl acetate 19:1) to give pale yellow coloured liquid as a mixture of two regio-isomers (22.78 g, 61.2 mmol, 90 %).

^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 3.65 (s, 3 H, C*H*$_3$O-C(O)-), 3.53-3.43 (m, 1 H, -C*H*-S-C(O)-CH_3), 2.30 (s, 3 H, -CH-S-C(O)-C*H*$_3$), 2.28 (t, 2 H, -C*H*$_2$-C(O)-OCH_3), 1.66-1.53 (m, 4 H, (-C*H*$_2$-)$_2$>CH-S-C(O)-CH_3), 1.52-1.42 (m, 2 H, -C*H*$_2$-CH_2-C(O)-OCH_3), 1.39-1.16 (m, 22 H, -C*H*$_2$, *aliphatic*-), 0.86 (t, 3 H, C*H*$_3$-$(CH_2)_n$-).

^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm): 196.08 (1 C, S-*C*(O)-CH_3), 174.24 (1 C, CH_3O-*C*(O)-), 51.39 (1 C, C(O)-O*C*H_3), 44.67 (1 C, *C*H-S-C(O)-), 34.76 (1 C, -*C*H_2-C(O)-OCH_3), 34.08 (2 C, (-*C*H_2-)$_2$>CH-S-C(O)-CH_3), 31.82 (1 C, -*C*H_2-CH_2-C(O)-OCH_3), 30.76 (1 C, -CH-S-C(O)-*C*H_3), 29.60 - 29.02 (5 C, -*C*H_2, *aliphatic*-), 26.74 - 26.65 (3 C, *C*H_2, *aliphatic*-), 24.89 - 22.64 (2 C, *C*H_2, *aliphatic*-), 14.07 (1 C, H, *C*H_3-$(CH_2)_n$-).

GC-MS: $[M]^+/z_{exp.}$ = 372.60, $[M]^+/z_{theo.}$ = 372.62

A.2.2 Synthesis of methyl 9(10)-mercaptostearate

In a representative procedure which was adopted from the literature,[3] 5.0 g of methyl 9(10)-(acetylthio)stearate (13.4 mmol, 1.0 eq.) were dissolved in ~11 mL of $MeOH_{anhydrous}$ (268.4 mmol, 20.0 eq.), and 10.0 mol-% of TBD (1.34 mmol, 0.186 g) were added to the reaction flask under inert gas at ambient temperature. Subsequently, the reaction mixture was refluxed (65 °C) under inert atmosphere for 7 hours. After removing the formed methyl acetate and the excess of methanol under reduced pressure, the residue was dissolved in 50 mL Et_2O, and washed respectively twice with distilled water and brine. The organic phase was dried over $MgSO_4$. After removal of the solvent under reduced pressure, the product (3.76 g, 11.4 mmol, 85 %) was isolated in a mixture of methyl 9(10)-mercaptostearate and the respective disulfide (82:18) as a light yellow liquid without further purification.

^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 3.66 (s, 3 H, C*H*$_3$O-C(O)-), 2.81- 2.72 (m, 1 H, -C*H*-SH), 2.64-2.55 (m, 2 H, -C*H*-S-S-C*H*-), 2.29 (t, 2 H, -C*H*$_2$-C(O)-OCH_3), 1.67-1.55 (m, 4 H, (-C*H*$_2$-)$_2$>CH-SH), 1.51-1.39 (m, 2 H, -C*H*$_2$-CH_2-C(O)-OCH_3), 1.39-1.16 (m, 22 H, -C*H*$_2$, *aliphatic*-), 0.87 (t, 3 H, C*H*$_3$-$(CH_2)_n$-).

^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm): 174.25 (1 C, CH_3O-*C*(O)-), 52.44 (2 C, -*C*H-S-S-*C*H-), 51.40 (1 C, C(O)-O*C*H_3), 41.14 (1 C, *C*H-SH), 34.76 (1 C, -*C*H_2-C(O)-OCH_3), 34.08 (2 C, (-*C*H_2-)$_2$>CH-SH), 31.86 (1 C, -*C*H_2-CH_2-C(O)-OCH_3), 29.60 - 29.02 (5 C, -*C*H_2, *aliphatic*-), 26.74 - 26.65 (4 C, *C*H_2, *aliphatic*-), 24.90 - 22.59 (2 C, *C*H_2, *aliphatic*-), 14.07 (1 C, H, *C*H_3-$(CH_2)_n$-).

GC-MS: $[M\text{-}SH]^+/z_{exp.}$ = 297.3, $[M]^+/z_{theo.}$ = 297.2

A.2.3 Synthesis of dimethyl 9(10),9'(10')-dithiodistearate (M1)

1.20 g of I_2 (4.72 mmol, 0.6 eq.) was dissolved in 37 mL of diethyl ether and 2.60 g of methyl 9(10)-mercaptostearate (7.87 mmol, 1.0 eq.) was added, subsequently the mixture was stirred at ambient temperature for 30 min. Afterwards, 0.32 g of NaOH (7.87 mmol, 1.0 eq.) dissolved in 18 mL of water was added, and stirring was continued overnight. To quench the reaction, 35 mL of diethyl ether was added, and then the mixture was extracted with an aqueous solution of sodium sulphite (10% w/w) until the organic layer was colourless. The aqueous layer was washed with additional 10 mL of diethyl ether, subsequently, the organic phases were combined and dried with $MgSO_4$. After removal of the solvent under reduced pressure, the product (2.36 g, 3.58 mmol, 91 %) was isolated as a light yellow liquid without further purification

^{1}H NMR (500 MHz, $CDCl_3$, δ in ppm): 3.63 (s, 6 H, C*H*$_3$O-C(O)-), 2.58-2.51 (m, 2 H, -C*H*-S-S-C*H*-), 2.27 (t, 4 H, -C*H*$_2$-C(O)-OCH_3), 1.64-1.45 (m, 12 H, (-C*H*$_2$-)$_2$>CH-S-S- and -C*H*$_2$-CH_2-C(O)-OCH_3), 1.39-1.16 (m, 44 H, -C*H*$_2$, *aliphatic*-), 0.87 (t, 6 H, C*H*$_3$-$(CH_2)_n$-).

^{13}C NMR (125 MHz, $CDCl_3$, δ in ppm): 174.14 (2 C, CH_3O-*C*(O)-), 52.32 (2 C, -*C*H-S-S-*C*H-), 51.31 (2 C, C(O)-O*C*H_3), 34.76 (2 C, -*C*H_2-C(O)-OCH_3), 34.08 (4 C, (-*C*H_2-)$_2$>CH-S-S-), 31.82 (2 C, -*C*H_2-CH_2-C(O)-OCH_3), 29.62 - 29.03 (10 C, -*C*H_2, *aliphatic*-), 26.73 - 26.62 (8 C, *C*H_2, *aliphatic*-), 24.84 - 22.56 (4 C, *C*H_2, *aliphatic*-), 14.07 (2 C, H, *C*H_3-$(CH_2)_n$-).

ESI-MS: [**M1**+Na^+]/z_{exp}. = 681.4915, [**M1**+Na^+]/z_{exp}. = 681.4931.

A.3. Polymerization of M1 with M2

The polymerizations were performed in a round bottom flask at 120 °C applying continuous inert gas flow. Monomers **M1** (350.0 mg, 0.53 mmol) and **M2** (62.75 mg, 0.53 mmol) were polymerized with the respective amount of the catalyst, i.e. TBD (1.0, 5.0 or 10.0 mol-% relative to **M1**) for 14 hours. ***Importantly***, prior to the addition of TBD, 2µmol-% hydroquinone was added to the monomer mixture. At the end of the specified reaction time, the polymerizations were cooled down to the ambient temperature, and dissolved in the smallest amount in THF. Subsequently, the crude polymers were purified via three-fold precipitation into ice-cold methanol. Polymer **P1**: sticky, brown solid, (0.32 g, 80.5 %)

$M_{n,\,GPC}$ = 13 500 g·mol^{-1}, $Đ$ = 1.8, DP_{NMR} = 28 (according *Formula 1* in Section B.1.)

$M_{n,\,NMR}$ = 19 950 g·mol^{-1} (according *Formula 2* in Section B.1.)

For in-depth additional characterization of **P1** refer to Fig 2-5 in the Main Text.

A.4. Synthesis of a proof-of-concept molecule (M1_S_x) via organocatalytic sulfur exchange reactions of M1 with elemental sulfur

181.2 mg of **M1** (0.275 mmol, 1.0 eq.) were mixed with 70.5 mg elemental sulfur (0.275 mmol, 1.0 eq.) in round bottom flask. The mixture was deoxygenated via purging with inert gas for 30 min. Subsequently, 2.0 mol-% TBD was added, and the mixture was heated to 135 °C. The reaction was performed for 1 h. Afterwards, to quench the reaction, the reaction flask was exposed to ambient atmosphere and cooled to ambient temperature. Consequently, 35 mL of DCM was added, and then the mixture was extracted with an aqueous solution of sodium sulfite until the organic layer was colourless. The aqueous layer was washed with additional 10 mL of DCM, subsequently, the organic phases were combined and dried with $MgSO_4$. After removal of the solvent under reduced pressure, the product was isolated quantitatively as an orange yellow liquid without further purification.

For in-depth analytical characterization of **M1_S_x** refer to Fig S13, 14 and 15, respectively in the Supporting Information.

A.5. Organocatalytic sulfur exchange reactions of P1 with elemental sulfur:

A.5.1. In stoichiometric manner with 100.0 mol-% S_8: The reaction was performed in similar manner as for **M1**. Respectively, 25.7 mg of **P1** (0.036 mmol, 1.0 eq.) were mixed with 9.25 mg elemental sulfur (0.036 mmol, 1.0 eq.) in round bottom flask. The mixture was deoxygenated via purging with inert gas for 30 min. Subsequently, 2.0 mol-% TBD was added, and the mixture was heated to 135 °C. The reaction was performed for 1 h. Afterwards, to quench the reaction, the reaction flask was exposed to ambient atmosphere and cooled to ambient temperature. Consequently, 5 mL of DCM was added, and then the mixture was extracted with an aqueous solution of sodium sulfite until the organic layer was colourless. The aqueous layer was washed with additional 5 mL of DCM, subsequently, the organic phases were combined and dried with $MgSO_4$. After removal of the solvent under reduced pressure, the product was isolated quantitatively as an orange highly viscous material without further purification.

A.5.1. Upon addition of incremental amounts of 5.0 mol-% S_8: The reaction was performed in similar manner as for **M1**, unless the addition of elemental sulfur was performed in incremental manner. Hence, 25.7 mg of **P1** (0.036 mmol, 1.0 eq.) were mixed with 5.0 mol-% elemental sulfur (0.46 mg 0.0018 mmol) in round bottom flask. The mixture was deoxygenated via purging with inert gas for 30 min. Subsequently, 2.0 mol-% TBD was added, and the mixture was heated to 135 °C. The reaction was performed for 1 h. Afterwards, in intervals of 30 min, 5.0 mol-% elemental sulfur was added, until a degradation of the polymeric product was detected via SEC analyses. To quench the reaction, the reaction flask was exposed to ambient atmosphere and cooled to ambient temperature. Consequently, 5 mL of DCM was added, and then the mixture was extracted with an aqueous solution of sodium sulfite until the organic layer was colourless. The aqueous layer was washed with additional 5 mL of DCM, subsequently, the organic phases were combined and dried with $MgSO_4$. After removal of the solvent under reduced pressure, the product was isolated quantitatively as an orange highly viscous material without further purification.

B. Measurements and analytical methods

B.1. Nuclear magnetic resonance (NMR) spectroscopy

NMR measurements were performed on a Bruker AM 400 (^{1}H: 400 MHz, ^{13}C: 100 MHz) spectrometer and Bruker Avance 500 (^{1}H: 500 MHz, ^{13}C: 125 MHz) equipped with Ultrashield magnets spectrometer. The δ-scale was referenced to the respective residual solvent signal of chloroform-d_1 which was employed as deuterated solvent: 7.26 ppm (^{1}H NMR) and 77.00 ppm (^{13}C NMR), respectively. For the analysis of the polymers the number of scans was set to 256 (^{1}H NMR) and 2048 (^{13}C NMR) scans, respectively. All NMR data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet), coupling constant(s) in Hertz (Hz) and integration. Multiplets (m) were reported over the range (ppm) where they appeared at the indicated field strength. In order to calculate the degree of polymerization (*DP*) and $M_{n,NMR}$ of the polymers, we took advantage of the ratio of the proton resonances in the ^{1}H NMR associated with the end groups (E_1,E_2) compared to the proton resonances of the methylene units -OC(O)O-CH_2-$(CH_2)_7$- of the polymer chain in the ^{1}H NMR spectra shown in Fig. 3 (in the Main Text).

E_1: C***H*****$_3$**-O end-group signals at 3.67 ppm (s)

E_2: ***H***O-end-group at 3.64 ppm (m)

Thus, the degree of polymerization (*n*, *DP*) was calculated using the integrals of the proton resonances of each end group: **A** and **B** are respectively the integral values of the resonances associated with end groups $\mathbf{E_1}$ and $\mathbf{E_2}$. Additionally, **P** is the integral value associated with the proton resonances of the α–methylene units -C***H*****$_2$**-C(O)O-CH_2- (2.28 ppm, indicated as a in Fig. 3) of the polymer chain in the ^{1}H NMR spectra:

$$n = DP = (4 \cdot \mathbf{P}) / [(\mathbf{A} + \mathbf{B}) \cdot 2] \qquad \textbf{\textit{Formula 1}}$$

The theoretical and experimental molecular weight for the polymer collated were calculated using the following equation (where M_{M1} = 659.13 g·mol^{-1}, M_{M2} = 118.18 g·mol^{-1} and M_{MeOH} = 32.04 g·mol^{-1} are the molecular weights of **M1**, **M2** and methanol, respectively):

$$M_{n,theor} = M_{n,NMR} = n \cdot (M_{M1} + M_{M2}) - 2n \cdot M_{MeOH} \qquad \textbf{\textit{Formula 2}}$$

B.2. Diffusion-ordered spectroscopy (DOSY NMR)

DOSY experiments based on ^{1}H NMR were performed in $CDCl_3$ (c = 8.9 mg mL^{-1}) at 298.00 K on a Bruker AM 400 spectrometer at an operating frequency of 400 MHz (^{1}H) using a stimulated echo sequence incorporating bipolar gradient pulses and a longitudinal eddy current delay (BPP-LED) with

the standard Bruker pulse program, ledbpgp2s. The gradient strength was linearly incremented in 96 steps from 5 % up to 95 % of the maximum gradient strength. Diffusion times and gradient pulse durations were optimized for each experiment in order to achieve a 95% decrease in the signal intensities at the largest gradient amplitude. After Fourier transformation and phase correction, the diffusion dimension of the 2D DOSY spectra was processed by means of the Bruker Topspin software package (version 3.2), and analyzed with the Bruker Dynamic Center. Spectra for the polymer and the corresponding single-chain nanoparticle were measured and mean values were taken from the experimentally determined diffusion coefficients *D* of the characteristic NMR-peaks. The hydrodynamic diameter *d* was obtained *via* the application of the Stokes-Einstein equation (with $k_B = 1.38 \cdot 10^{-23}$ m^2 kg s^{-2} K^{-1}, T = 298 K, η = 0.536mPa s, d = diameter, D = diffusion coefficient)

$$d = \frac{k_B T}{3 \pi \eta D} \qquad \textbf{\textit{Formula 3}}$$

B.3. Size exclusion chromatography (SEC)

The apparent number average molar mass (M_n) and the molar mass distribution [$Đ$ (polydispersity index) = M_w/M_n] of the polymers were determined via SEC measurements, which were performed on:

a) **SEC_1:** A Polymer Laboratories (Varian) PL-GPC 50 Plus Integrated System, comprising an autosampler, a PLgel 5mm bead-size guard column (50 × 7.5 mm), one PLgel 5mm Mixed E column (300 × 7.5 mm), three PLgel 5mm Mixed C columns (300 × 7.5 mm) and a differential refractive index detector using tetrahydrofuran (THF) as the eluent at 35 °C with a flow rate of 1.0 mL min^{-1}. The SEC system was calibrated using linear polymethacrylate (PMMA) standards ranging from 700 to $2.0 \cdot 10^6$ g mol^{-1}. Calculation of the molecular weight proceeded via the Mark-Houwink-Sakurada (MHS) parameters for PMMA in THF at 35 °C, i.e., $K = 12.8 \cdot 10^{-3}$ mL·g^{-1}, $\alpha = 0.69$.

b) **SEC_2**: A TOSOH Eco-SEC HLC-8320 GPC system, which comprised an autosampler, a SDV 5 µm bead size guard column (50 × 8 mm, PSS) followed by three SDV 5 µm columns (300 × 7.5 mm, subsequently 100, 1000, and 10^5 Å pore size, PSS), a differential refractive index (DRI) detector, and UV-Vis detector set to 254 nm, with THF as the eluent at 35 °C with a flow rate of 1.0 mL·min^{-1}. The SEC system was calibrated by using linear PMMA standards ranging from 800 to 1.82 × 10^6 g mol^{-1}. Calculation of the molar mass proceeded by using a relative calibration based on PMMA standards by utilizing the Mark-Houwink-Sakurada (MHS) parameters for PMMA in THF at 30 °C, i.e., $K = 12.8 \cdot 10^{-3}$ mL·g^{-1}, $\alpha = 0.688$.[4]

The polymer samples were dissolved at a concentration of 2.0 mg mL^{-1}in aforementioned eluent and filtered over a 0.2µm filter prior to the measurement.

B.4. High resolution/orbitrap electrospray ionization mass spectrometry (ESI-MS)

Mass spectra were recorded on a Q Exactive (Orbitrap) mass spectrometer (Thermo Fischer Scientific, San Jose, CA, USA) equipped with a HESI II probe. The spectra were recorded in positive mode and the analyte was dissolved in a THF/MeOH solution (3:2, doped with 100 µmol sodium trifluoroacetate, c = 0.01 g mL^{-1}). The instrument was calibrated in the m/z range 74 to 1822 using premixed calibration solutions (Thermo Scientific). The Fourier-Transform resolution was set to 140 000. A constant spray voltage of 3.6 kV and a dimensionless sheath gas of 5 were applied. The capillary temperature and the S-lens RF level were set to 320 °C and 68.0, respectively. The flow rate was set to 5 $\mu L \cdot min^{-1}$

B.5. Gas chromatography-mass spectrometry (GC-MS)

GC-MS (EI) chromatograms were recorded using a Varian 431 GC instrument with a capillary column FactorFourTM VF-5 ms (30 m × 0.25 mm × 0.25 µm) and a Varian 210 ion trap mass detector. Scans were performed from 40 to 650 m/z at rate of 1.0 scans × s^{-1}. Method A - the oven temperature program was: initial temperature 95 °C, hold for 1 min, ramp at 15 $°C \cdot min^{-1}$ to 200 °C, hold for 2 min, ramp at 15 $°C \cdot min^{-1}$ to 325 °C, hold for 5 min. Method B - the oven temperature was: initial 35 °C, hold for 2 min, ramp at 10 $°C \cdot min^{-1}$ to 150 °C, hold for 1 min. The injector transfer line temperature was set to 250 °C. Measurements were performed in split–split mode (split ratio 50 : 1) using helium as the carrier gas (flow rate 1.0 $mL \cdot min^{-1}$).

B.6. Attenuated total reflectance infrared spectroscopy (ATR-IR)

All IR measurements were performed on a Bruker Alpha ATR-IR Spectrometer with a range of 500 to 4000 cm^{-1} at ambient temperature.

B.7. Differential scanning calorimetry (DSC)

DSC 1 STAR^e system (Mettler Toledo) calorimeter with autosampler under a constant nitrogen flow of 10 $mL \cdot min^{-1}$ using 100 µL aluminum crucible was utilized for DSC analysis. For analysis the following method was employed: the first heating proceeded from -85 °C to 200 °C at a heating rate of 20 $°C \cdot min^{-1}$; a cooling step was performed from 200 °C to -85 °C at a heating rate of 20 °C; the second heating run was recorded from -85 °C to 200 °C at a heating rate of 20 $°C \cdot min^{-1}$. The melting temperature, T_m, is reported as the minimum of the endothermic peak of the second heating scan unless annealing was used as a pretreatment. The glass transition temperature, T_g, is reported as the midpoint of the step change of

the heat capacity in the second heating scan. Measurements were performed with samples in the range of 5-20 mg.

B.8. Ultraviolet-visible (UV-Vis) spectroscopy

The UV-Vis spectra were recorded on a Cary 100 UV-Visible Spectrophotometer (Agilent Technologies, USA) equipped with a tungsten halogen light source (190 to 900 nm, accuracy +/- 2 nm) and a R928 PMT detector. Spectra were recorded in THF at 20 °C with a concentration of $1.23 \cdot 10^{-5}$ mmol mL^{-1} and $6.25 \cdot 10^{-2}$ mg mL^{-1} for monomer, the respective polymer and high sulfur content polymer derivatives, respectively, and collected between 200 and 800 nm. Samples were baseline corrected with respect to the pure solvent.

B.9. Elementary analysis (C/H/N/S)

Elemental analysis characterization was performed with an Elementar Vario EL device (Elementar, Germany).

C. Additional data, figures and tables

C.1. Characterization of M1

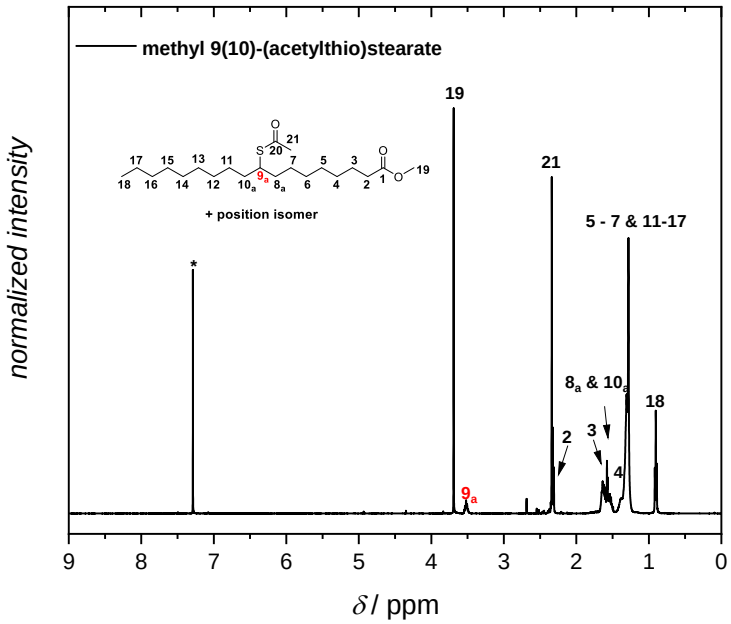

Figure S1 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of methyl 9(10)-(acetylthio)stearate. The magnetic resonance marked with an * is assigned to $CHCl_3$.

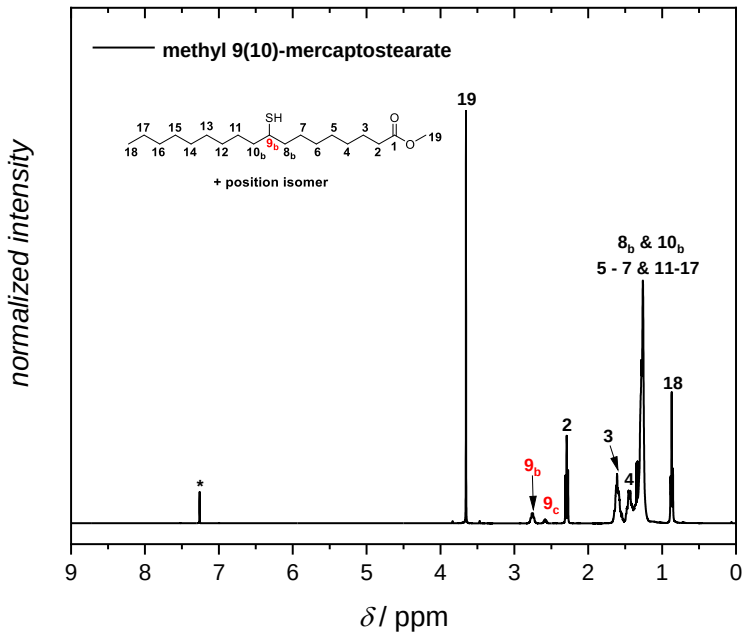

Figure S2 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of methyl 9(10)-mercaptostearate. The magnetic resonance marked with an * is assigned to $CHCl_3$, and $\mathbf{9_c}$ to methanetriyl group of **M1**, respectively.

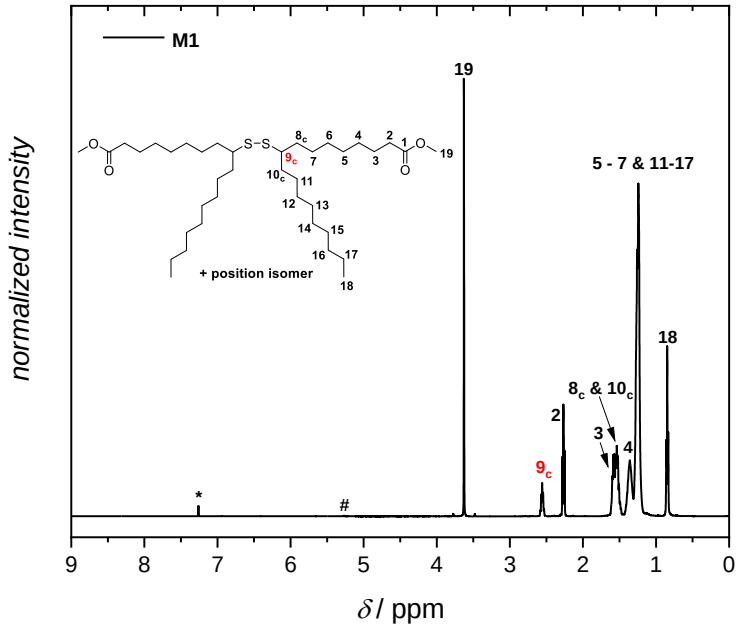

Figure S3 ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **M1**. The magnetic resonance marked with an * is assigned to $CHCl_3$, and a # to residual DCM, respectively.

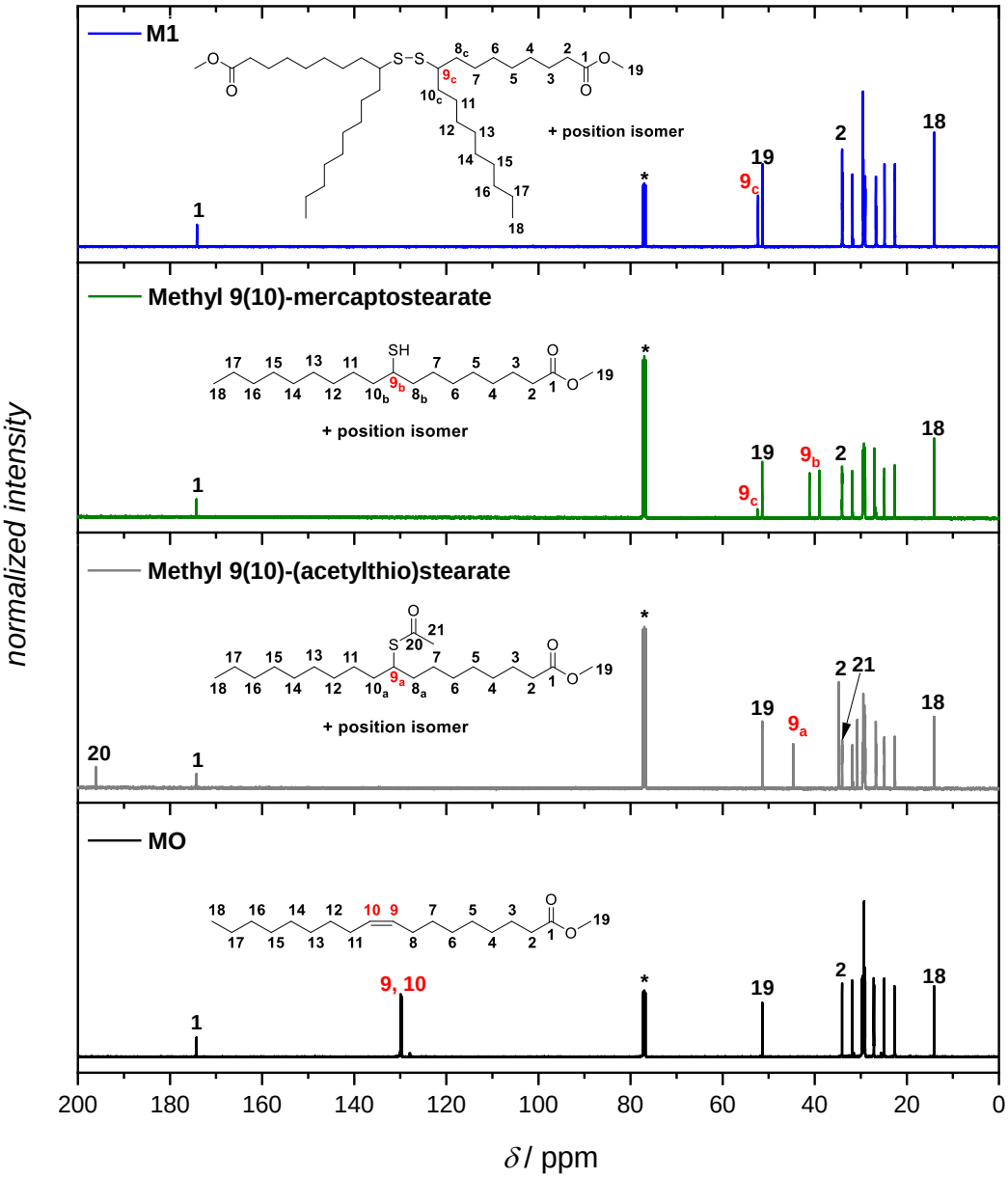

Figure S4 ^{13}C NMR spectra ($CDCl_3$, 298 K) of **M1** (125 MHz, blue), methyl 9(10)-mercaptostearate (100 MHz, olive green), methyl 9(10)-(acetylthio)stearate (100 MHz, grey) and methyl oleate (100 MHz, MO, black, respectively. Critical magnetic resonances are assigned with the respective numbers. The magnetic resonance marked with an * is assigned to $CHCl_3$.

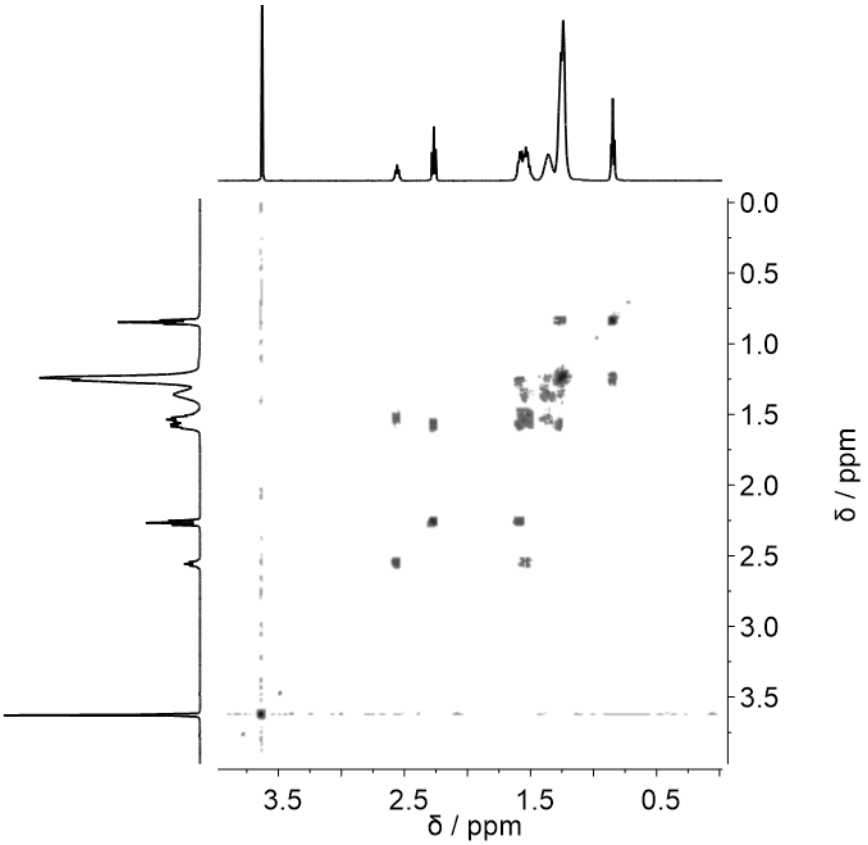

Figure S5 2D ^{1}H-^{1}H COSY spectrum (500 MHz, $CDCl_3$, 298 K) of **M1.**

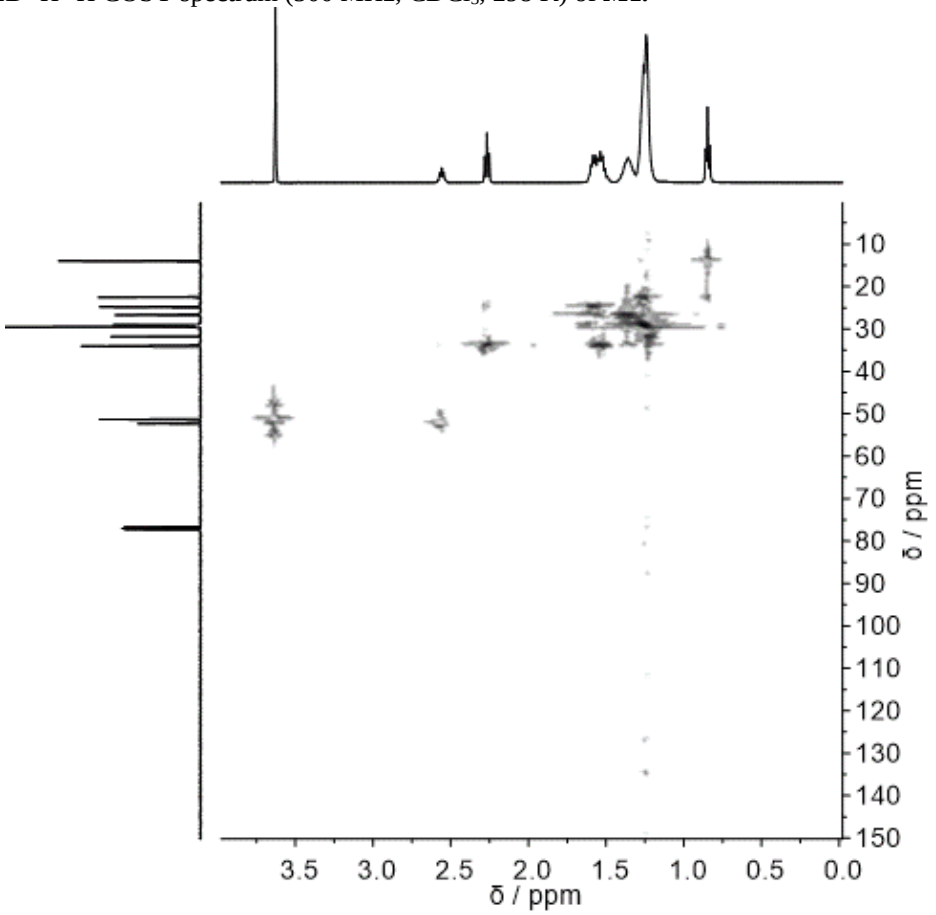

Figure S6 2D HSQC spectrum (500 MHz, $CDCl_3$, 298 K) of **M1.**

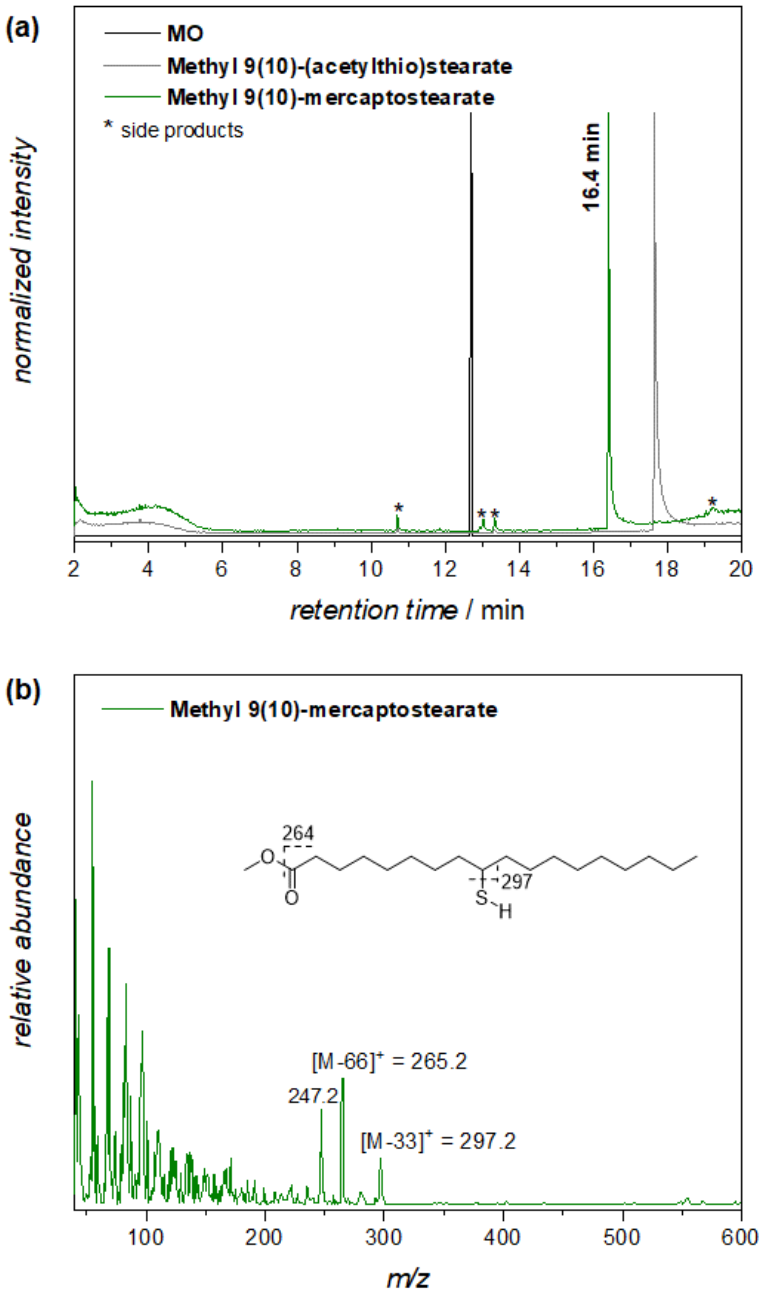

Figure S7 (a) Comparative GC-MS spectra of methyl oleate (MO, black), methyl 9(10)-(acetylthio)stearate (grey) and methyl 9(10)-mercaptostearate (olive green), respectively; (b) mass spectrum of methyl 9(10)-mercaptostearate.

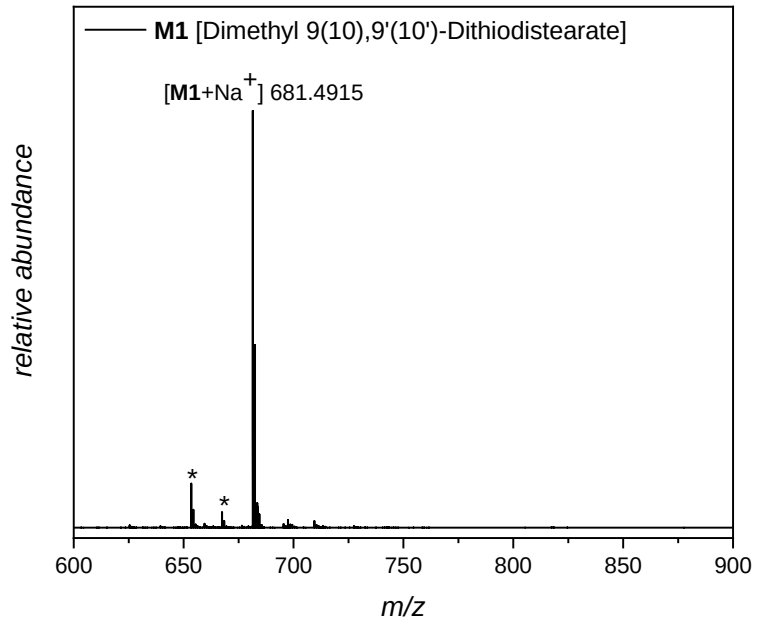

Figure S8 High resolution ESI-MS analysis of **M1**. The signals marked with an asterisk are assigned to background signals.

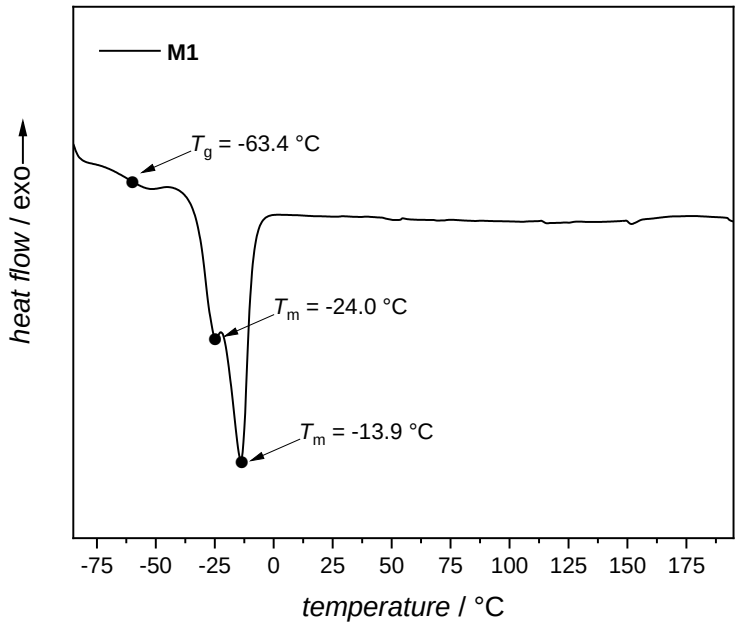

Figure S9 Exemplary DSC graph (second heating scan) of **M1**.

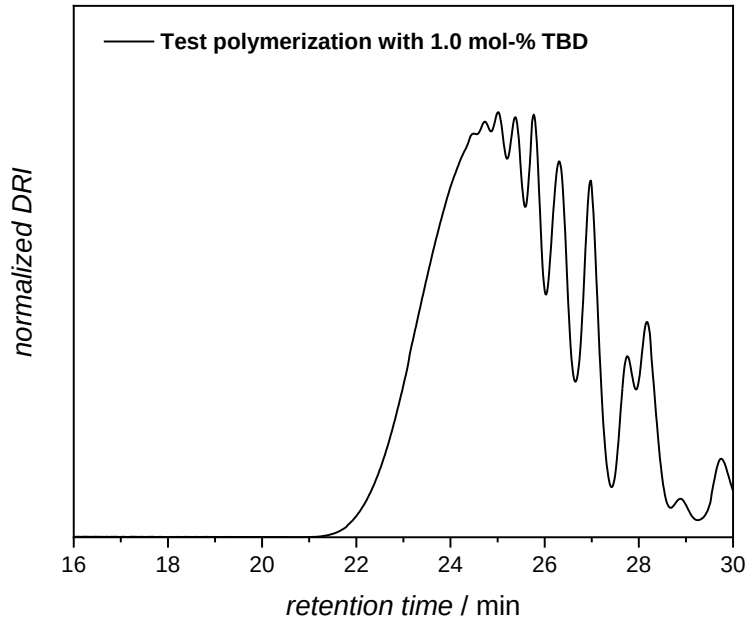

Figure S10 SEC chromatograms obtained via system **SEC_2** in THF for the polymerization of monomer **M1** with **M2** in the presence of 1.0 mol-% TBD, resulting in oligomerization.

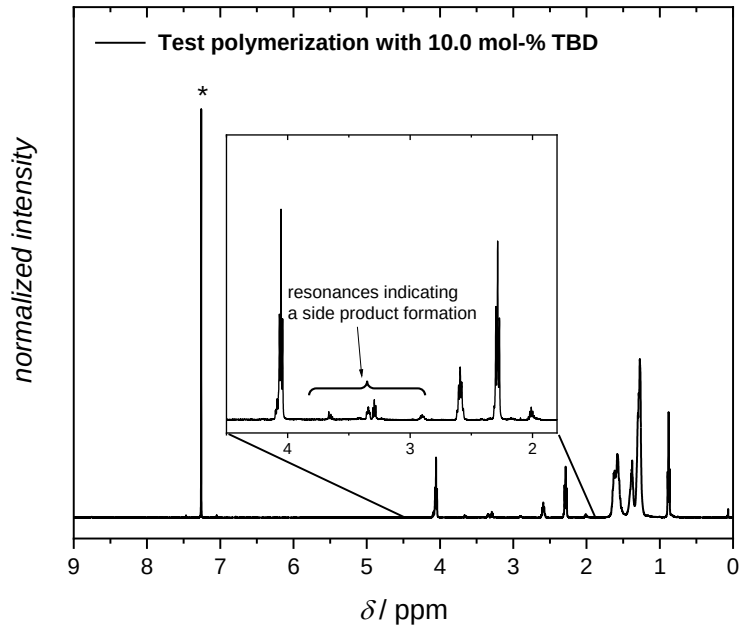

Figure S11 ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of the crude the polymerization mixture of monomer **M1** with **M2** in the presence of 10.0 mol-% TBD, resulting in side reactions.

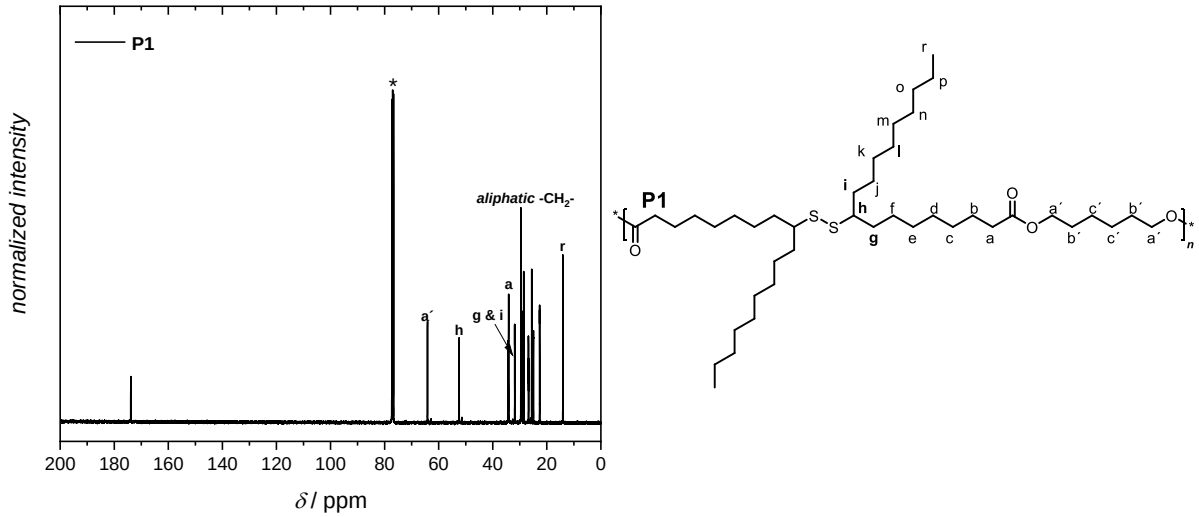

Figure S12 ^{13}C NMR spectra (125 MHz, $CDCl_3$, 298 K) of **P1** (above) and the chemical structure of the polymer, which critical magnetic resonances are assigned with the respective letters (bottom). The magnetic resonance marked with an * is assigned to $CHCl_3$.

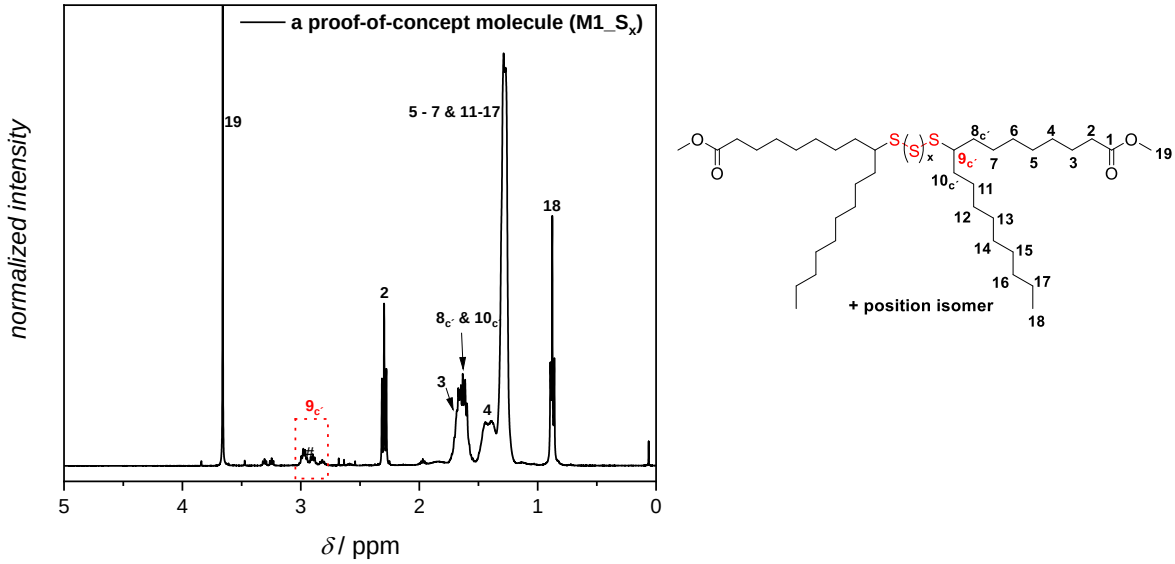

Figure S13 ^{1}H NMR spectra (500 MHz, $CDCl_3$, 298 K) of a proof-of-concept molecule (**M1_S$_x$**) (above) and the respective chemical structure that is assigned with the critical magnetic resonances (bottom).

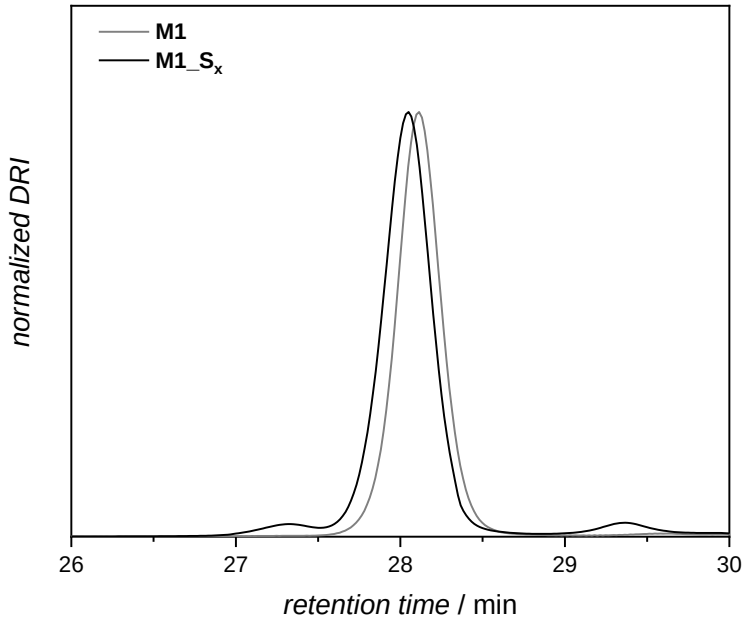

Figure S14 SEC chromatograms obtained via system **SEC_2** in THF for monomer **M1** and a proof-of-concept molecule (**M1_Sx**).

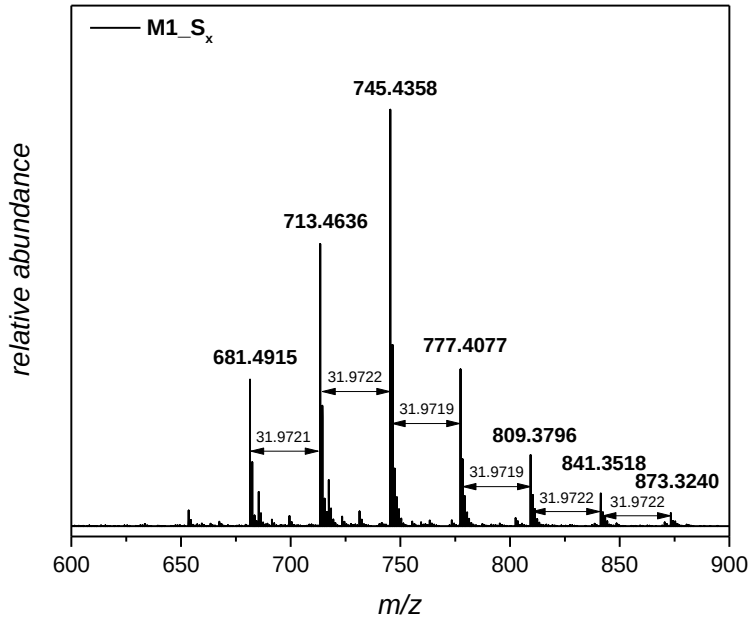

Figure S15 High resolution ESI-MS analysis of a proof-of-concept molecule, **M1_Sx**.

Table S1 The **TBD** mediated organocatalytic sulfur exchange reactions of **P1** with elemental sulfur.

Entry	*Sample code*	*Feed ratio of S_8* *(mol-% /repetaing unit)*	*TBD* *(mol-%/ repeating unit)*	*M_n*[c] *(g·mol^{-1})*	*Isolated yield*[d] *(%)*
1[a]	**P1_S_100.0 mol-%**	100.0	2.0	12 500	78 %
2[b]	**P1_S_5.0 mol-%**	5.0	2.0	13 900	-[e]
3[b]	**P1_S_25.0 mol-%**	25.0	-	14 300	-[e]
4[b]	**P1_S_35.0 mol-%**	35.0	-	14 500	-[e]
5[b]	**P1_S_70.0 mol-%**	70.0	-	14 600	92
6[b]	**P1_S_75.0 mol-%**	75.0	-	11 600	65

a. S_8 was added in stoichiometric manner (i.e. 100.0 mol-% of S_8 was added at the beginning of the reaction.
b. The reaction was performed in one-pot, thus it was started with 5.0 mol-% S_8, and consequently 5.0 mol-% of S_8 were added *in situ* in incremental manner to the reaction mixture in each 30 min.
c. Determined by SEC relative to polymethacrylate standards in THF as eleunt.
d. Isolated yield was calculated gravimetrically.
e. Sample was not isolated.

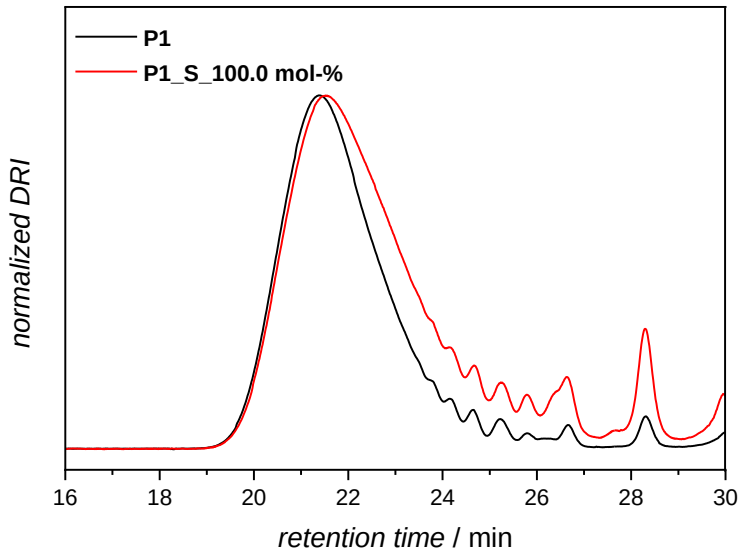

Figure S16 SEC chromatograms obtained via system **SEC_2** in THF for polymer **P1** and **P1_S_100.0 mol-%.**

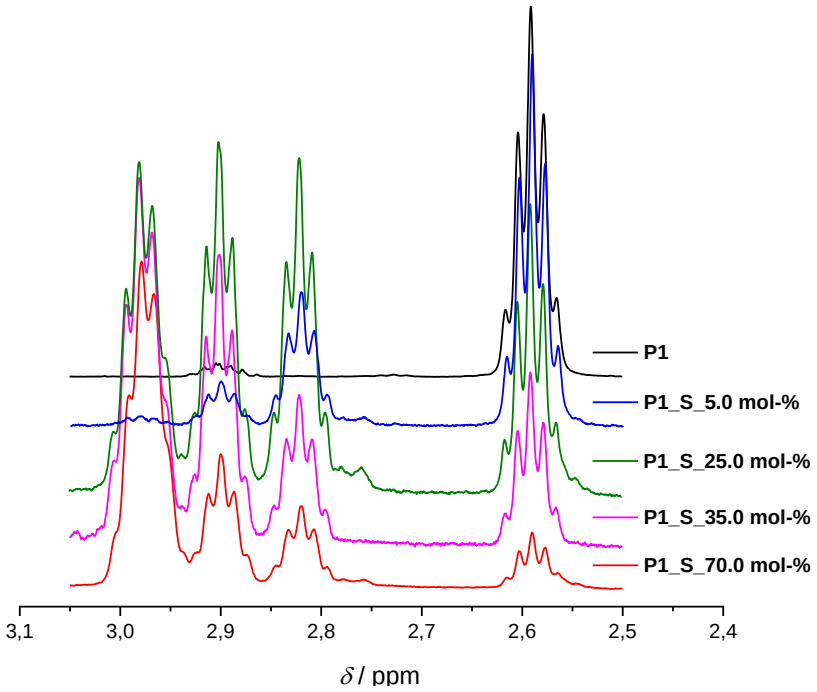

Figure S17 Magnified view of ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) of the 3.1 – 2.4 ppm range for chemical shifts before and after the organocatlytic sulfur exchange reaction of **P1** with different aliquots of S_8.

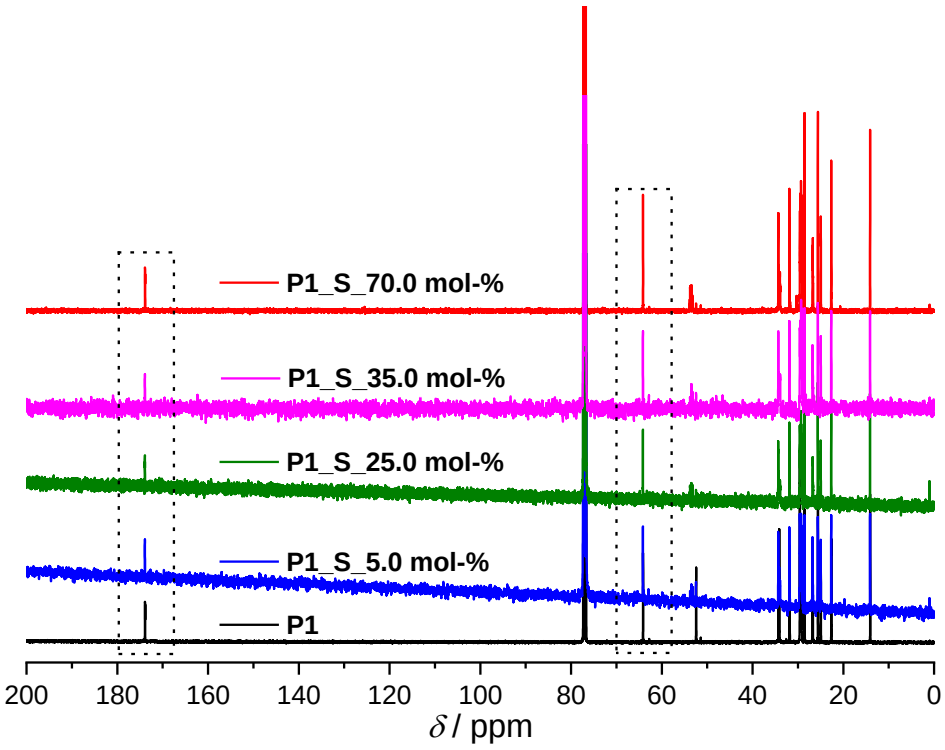

Figure S18 The comparative analysis of ^{13}C NMR spectra (100 MHz, $CDCl_3$, 298 K) of the crude reaction mixtures after 5.0, 25.0, 35.0 and 70.0 mol-% addition of S_8 aliquots to **P1** indicating that the ester functional moiety remained intact (refer to 173.9 ppm and 64.2 ppm, respectively), and the polymer did not undergo any depolymerization via thioesterification as one could have expected.

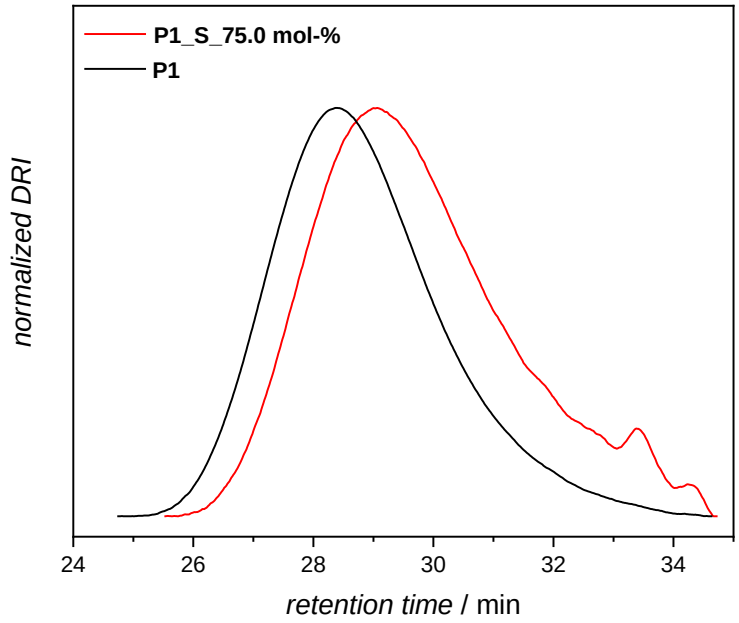

Figure S19 SEC chromatograms obtained via system **SEC_1** in THF for polymer **P1** and **P1_S_75.0 mol-%**.

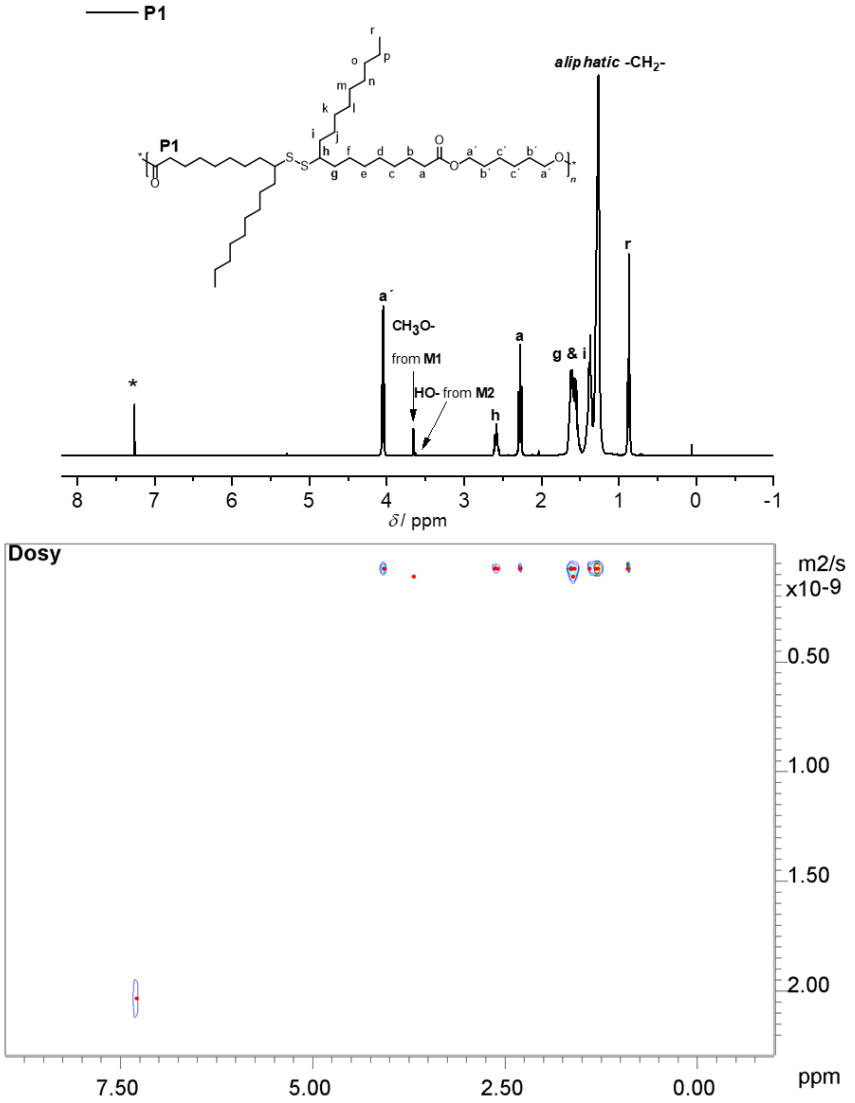

Figure S20 DOSY spectrum (400 MHz, $CDCl_3$, 298 K) of **P1**.

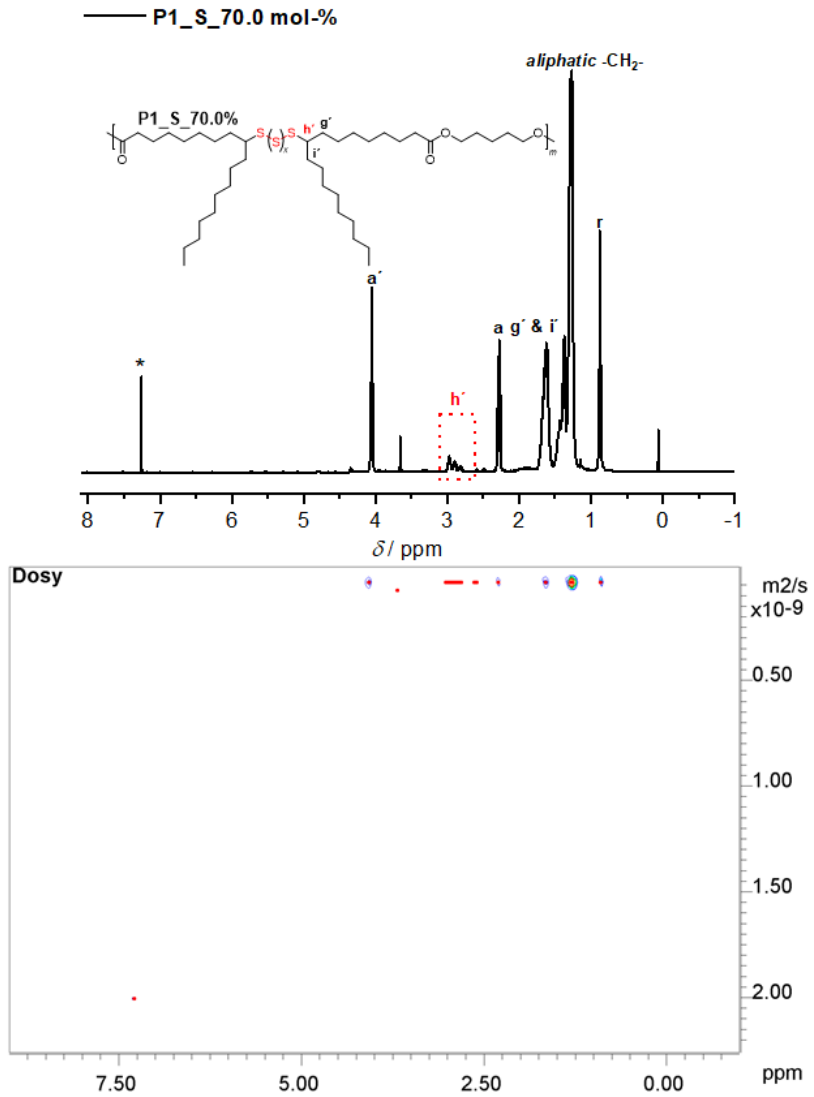

Figure S21 DOSY spectrum (400 MHz, $CDCl_3$, 298 K) of **P1_S_70.0 mol-%.**

Table S2 DOSY NMR (400 MHz, $CDCl_3$, 298 K) results of **P1** and **P1_S_70.0 mol-%** including diffusion coefficients and diameter of three signals.

Species	***Diffusion Coefficient D*/ m^2s^{-1}**	***Signal*/ ppm**	***Diameter d*/ nm**
P1	$1.22\ 10^{-10}$	4.08	6.67
	$1.21\ 10^{-10}$	2.63	6.73
	$1.24\ 10^{-10}$	2.31	6.56
P1_S_70.0 mol-%	$6.58\ 10^{-11}$	4.08	12.38
	6.8710^{-10}	2.63	11.86
	$7.06\ 10^{-10}$	2.31	11.53

D. References

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