

Supporting Information for Cross-Me- tathesis of Technical Grade Methyl Oleate for the Synthesis of Bio-based Polyesters and Polyamides

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1. General considerations

Commercially available solvents (HPLC grade) and reagents were used as received unless stated otherwise. Dichloroethane was degassed by bubbling nitrogen gas for 15 min. and stored in N₂ protective atmosphere over activated 4 Å molecular sieves for at least 12 h prior to use.

Technical grade methyl oleate was pretreated with distillation from activated Al₂O₃ at 1 mbar pressure two times consecutively and stored under nitrogen protective atmosphere over activated Al₂O₃. Commercially available catalysts **Ru3** – **Ru6** were used as received. Olefin metathesis reactions were quenched using commercially available compound **S-1**.¹ Commercially available Ti(O^{*i*}Bu)₄, 1,8-diaminooctane and diol comonomers were used as received.

The NMR spectra were recorded at 22 ± 2 °C using an Ultrashield III spectrometer of 300 MHz manufactured by Bruker. Chemical shifts are reported in parts per million (ppm) and referenced against the residual proton of a solvent: CDCl₃ (¹H = 7.26 ppm, ¹³C = 77.16 ppm). Coupling constants J are given in hertz (Hz). Data are reported as follows: chemical shift, multiplicity, coupling constant, integration.

GC measurements were conducted on Shimadzu GC-2014 chromatograph equipped with SLB™ 5ms capillary column.

Thermogravimetric analyses were performed on a TGA/DSC1 manufactured by Mettler-Toledo to determine the degradation temperatures and mass losses of the materials synthesized oligomers. Such temperatures were determined based on the onset point of the slope of the thermogravimetric curve. The equipment is calibrated yearly for temperatures using nickel (purity > 99.99%) as a reference standard. The samples of around 15 mg were placed in open alumina crucibles and were submitted to heating ramps of 10 °C/min from room temperature to 700 °C using 50 mL/min of nitrogen as atmosphere. The experimental error supplied by the manufacturer is ± 3% for both temperature determination and weight.

Differential scanning calorimetry was recorded using a DSC2 from Mettler-Toledo in order to determine the melting and any other thermal phenomena of the samples from the obtained thermograms (heat flow vs temperature). Melting temperatures of oligomers were given by the onset point of the endothermic signals. The calibration of heat flow and temperature is carried out monthly by using high purity indium standard (purity > 99.99%), so the accuracy of the given temperatures of melting is about ± 0.6 °C. The enthalpies of melting are calculated by integration of the endothermic peaks assuming a linear baseline, and the accuracy of the determination is about ± 5%. The samples of around 10 mg were measured inside closed aluminum crucibles which were submitted to three cycles of heating/cooling at 5 °C/min from -80 °C to 300 °C in a controlled atmosphere of nitrogen.

2. Self-cross metathesis of methyl oleate

2. 1. Catalysts screening – general procedure

20 mL vial, equipped with magnetic stir bar, was charged with catalyst stock solution in dichloroethane (approximately 10 mg/mL). The amount of catalyst solution was adjusted to the catalyst loading. The solvent was removed in the flow of nitrogen and methyl oleate was added (1.73 g, 2 mL, 5.84 mmol). The vial was purged with nitrogen and closed with a screw cap. Reaction was stirred at 50 °C for 3 h. After that hexadecane stock solution (1.00 mL of 170 mg/mL) was added, followed with **S-1** (to quench the catalysis).¹ The sample was analyzed by gas chromatography.

20 mL vial, equipped with a magnetic stir bar, was charged with catalyst stock solution in dichloroethane (approximately 10 mg/mL). The amount of catalyst solution was adjusted to the catalyst loading. The solvent was removed in the flow of nitrogen and methyl oleate was added (1.73 g, 2 mL, 5.84 mmol). The vial was purged with nitrogen and closed with a screw cap. The reaction was stirred at 50 °C for 3 h. After that hexadecane stock solution (1.00 mL of 170 mg/mL) was added, followed by **S-1** (to quench the catalysis). The sample was analyzed by GC.

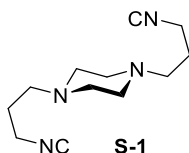


Figure S1. Compound **S-1** used to quench olefin metathesis reactions.

2. 2. Gas chromatography analysis

Gas chromatography was performed using following instrument setup:

Injector – split mode; temperature: 300 °C; split ratio 70:1.

Oven – 100 °C for 7 min.; then 10 °C/min. to 200 °C for 5 min.; then 15 °C/min to 240 °C for 5 min. and 15 °C/min. to 250 °C for 4.67 min.

Mobile phase – helium

Injection volume – 1 µL.

FID – temperature: 300 °C.

Three t0 samples were prepared (without addition of the catalyst). 1.73 g of the pretreated, technical grade methyl oleate was mixed with 1 mL of 170 mg/mL hexadecane stock solution in toluene and gas chromatogram was measured. The average area ratio of signals of methyl oleate **1(Z)** and methyl linoleate **2** to hexadecane was determined as 8.562. Conversion was calculated according to the following formula:

$$\text{Conv.} = 1 - \frac{A_{1(Z)+2}}{A_{\text{hexadecane}} \cdot 8.562}$$

$A_{1(Z)+2}$ – signal area of methyl oleate **1(Z)** and methyl linoleate **2**; $A_{\text{hexadecane}}$ – signal area of hexadecane.

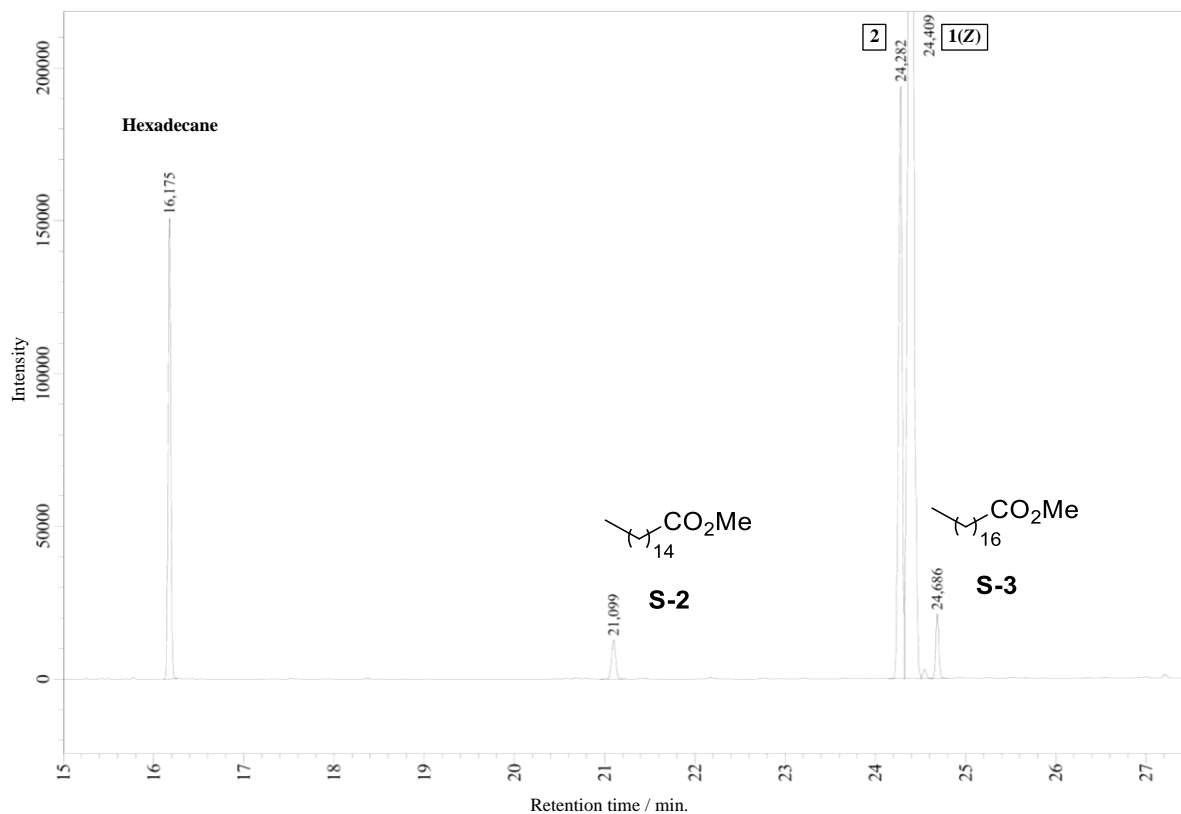


Figure S2. Gas chromatogram of substrate with added internal standard (hexadecane).

Three samples were prepared by mixing dimethyl octadec-9-enedioate (**3**) (88.8 mg, 190.4 mg and 366.4 mg) with 1 mL of 170 mg/mL hexadecane stock solution in toluene and gas chromatograms were measured.

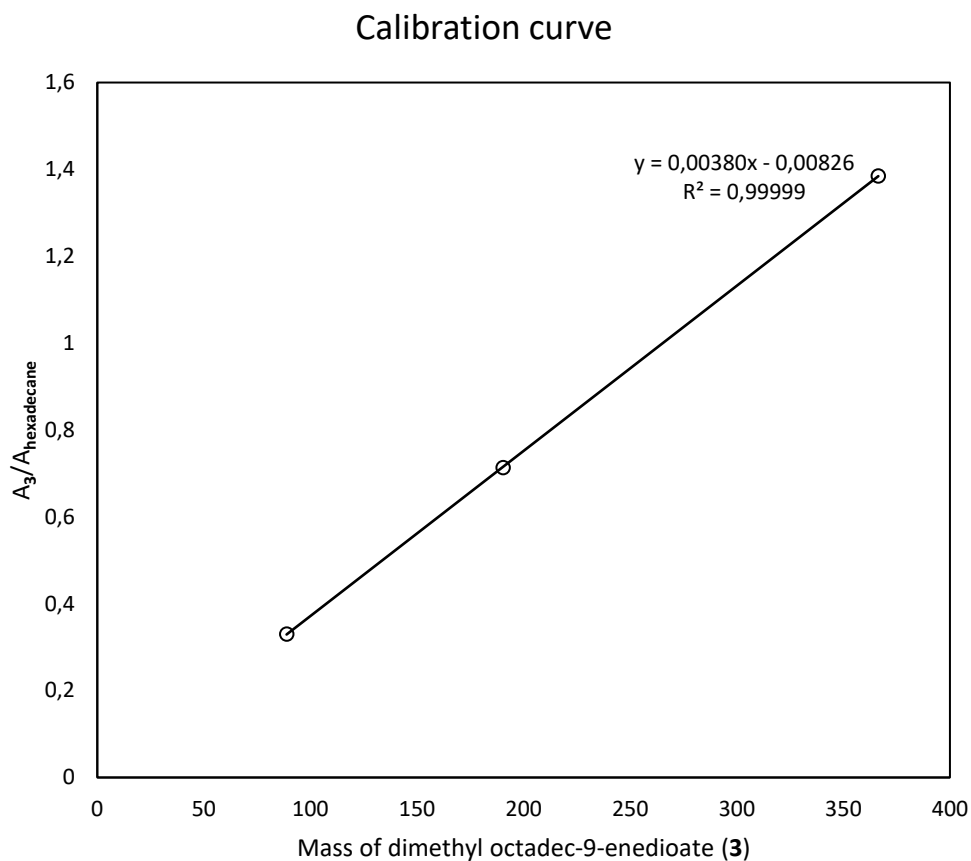


Figure S3. Calibration curve for dimethyl octadec-9-enedioate (**3**).

Yield was calculated according to the following formula:

$$\text{Yield} = \frac{m_3(\text{in sample})}{m_3(\text{theoretical})} = \frac{\left(\frac{A_3}{A_{\text{hexadecane}}} + 0.00826 \right) / 0.00380}{994.54}$$

A_3 – signal area of dimethyl octadec-9-enedioate (**3**); $A_{\text{hexadecane}}$ – signal area of hexadecane.

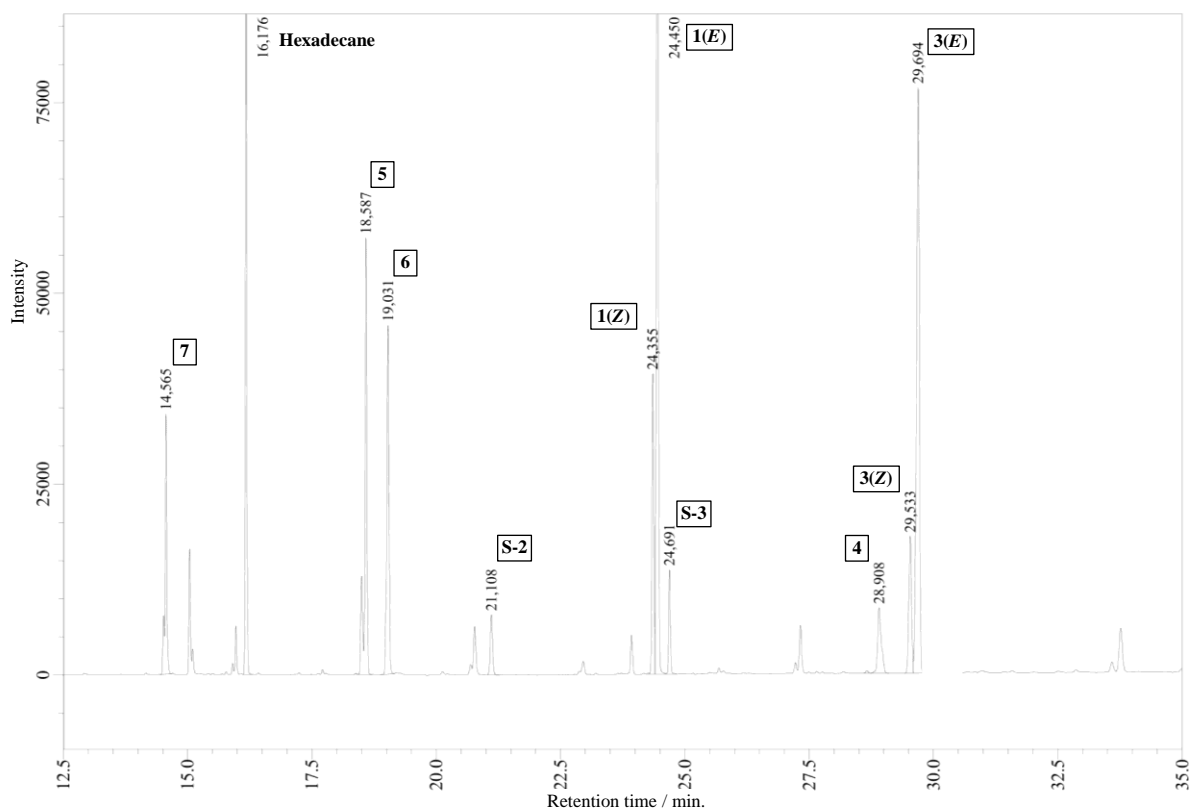
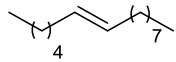
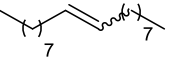
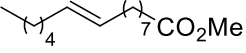
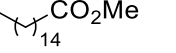
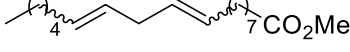
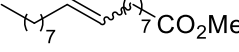
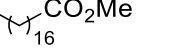
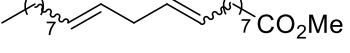
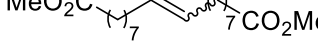


Figure S4. Gas chromatogram of exemplary crude reaction mixture.

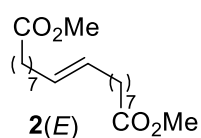
Table S1. Structures of compounds with their retention time.

Formula	Retention time (min.)
 7	14.565
Hexadecane	16.176
 5	18.587
 6	19.031
 S-2	21.108
 2	24.282
 1	24.355 (Z), 24.450 (E)
 S-3	24.691
 4	28.908
 3	29.533 (Z), 29.694 (E)

The compound formula was confirmed with the use of GC-MS.

2. 3. Synthesis of dimethyl *E*-octadec-9-enedioate 2

500 mL one necked flask, equipped with a magnetic stir bar, was charged with ca. 300 mL (249.58 g, 0.842 mol) of methyl oleate. Catalyst **Ru3** (52.8 mg, 84.2 μmol , 100 ppm) was added in a solid form and the atmosphere in the flask was exchanged to nitrogen using Schlenk technique. The content of the flask was stirred at 50 $^{\circ}\text{C}$ for 3 h. After that time, **S-1** (81.6 mg, 370.4 μmol , 440 ppm) was added in solid form and everything was stirred for 30 min. 1.7 g of SiO_2 (gel for column chromatography) was added and everything was stirred for overnight. SiO_2 was filtered of and washed with hexane. The product was isolated using fractional distillation. At 1 mbar pressure, the fraction containing product was collected at 172-192 $^{\circ}\text{C}$. The diester was further purified by crystallization from methanol at -30 $^{\circ}\text{C}$ and washed with ice cold methanol to afford 34.32 g of product as transparent crystals of 96.6 % purity. Further product crystallization from the supernatant gave 2nd crystallization crop – 21.57 g of 85.1 % purity. The amount of pure diester product in both crystallization crops corresponds to 51.51 g, 0.151 mol, total yield of 36 %. Analytical data match the previously reported for this compound.²



^1H NMR (300 MHz, CDCl_3) δ 5.37 (td, $J = 3.7, 1.8$ Hz, 2H), 3.66 (s, 6H), 2.30 (t, $J = 7.6$ Hz, 4H), 2.09 – 1.83 (m, 4H), 1.67 – 1.56 (m, 4H), 1.39 – 1.21 (m, 16H).

^{13}C NMR (75 MHz, CDCl_3) δ 174.5, 130.5, 51.6, 34.3, 32.7, 29.7, 29.3, 29.1, 25.1.

3. Polycondensation reactions

3. 1. General procedure

Into a 50 mL, round bottom flask $\text{Ti}(\text{O}^i\text{Bu})_4$ (10 mg, 29.4 μmol , 1 mol%), diester **3** (1.00 g, 2.94 mmol, 1 equiv.) and comonomer (number of equivalents varied, see Table S2) were placed. The content of the flask was stirred using magnetic stir bar and the temperature was elevated (oil bath heating) using following temperature program: 150 °C for 20 min.; then 160 °C for 20 min.; then 170 °C for 20 min.; then 180 °C for 20 min.; then 190 °C for 20 min.; then 200 °C for 20 min.; then 200 °C, N_2 purge for 20 min.; then 200 °C, vacuum (1 mbar, time varied, see Table S2). Stirring stopped after 2 h of the vacuum step. Reaction work up differ when oligomers and polymers were synthesized.

Work up for oligomers. The material was solubilized chloroform (10 mL) and precipitated with MeOH (100 mL). The brown material was washed with MeOH (3×100 mL) and dried under vacuum to give oligomers.

Work up for polymers. To the reaction flask 30 mL of chloroform was added and the flask was closed with a plastic stopper. The content of the flask was stirred at 80 °C for 15 min. After this procedure, the polymer was soaked with solvent and detached easier from flask walls. The content of the flask was stirred for additional 15 min. at 80 °C. The product was filtered off on a sintered funnel and washed with 30 mL of chloroform. Drying of the product under the reduced pressure of an oil pump (100 °C for 30 min.) afforded brown-orange jelly solid.

Table S2. Yields and conditions of synthesis of oligo- and polymers.

Entry	Polymer	Equivalents of comonomer	Vacuum time	Yield
1		4	30 min.	51 %
2		4	19 h	52 %
3		1.5	225 min.	76 %
4		1.5	21 h	81 %
5		1.2	180 min.	74 %
6		1.2	21 h	88 %
7		1.2	19 h	24 %
9		1.2	19 h	51 %

4. NMR spectra

4. 1. Dimethyl *E*-octadec-9-enedioate (**3(E)**)

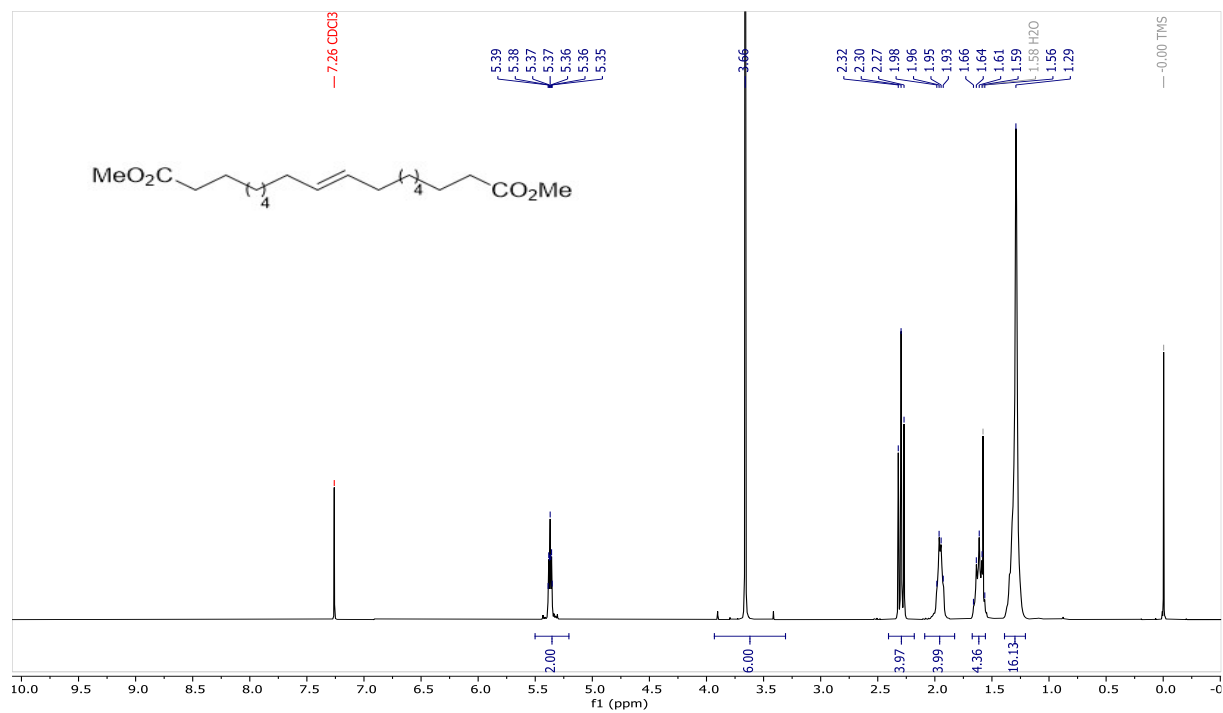


Figure S5. ¹H NMR spectrum of dimethyl *E*-octadec-9-enedioate (**3(E)**).

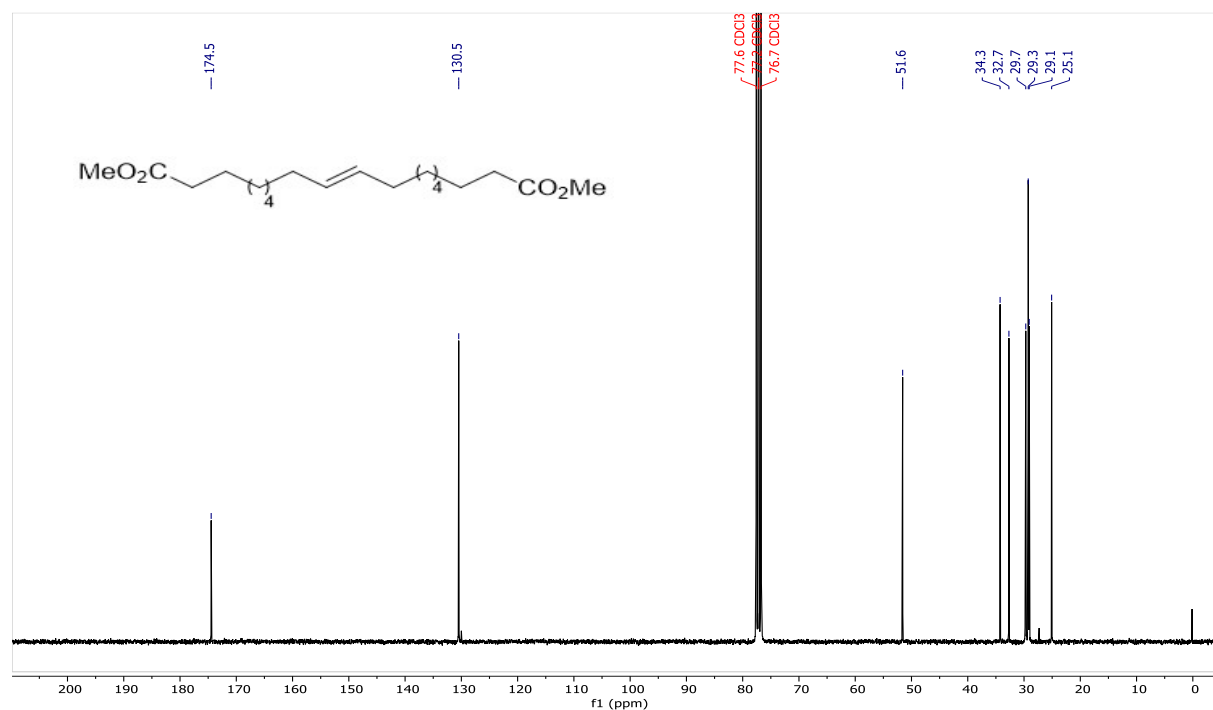


Figure S6. ¹³C NMR spectrum of dimethyl *E*-octadec-9-enedioate (**3(E)**).

4. 2. Oligomer with ethylene glycol (Table S2, Entry 1)

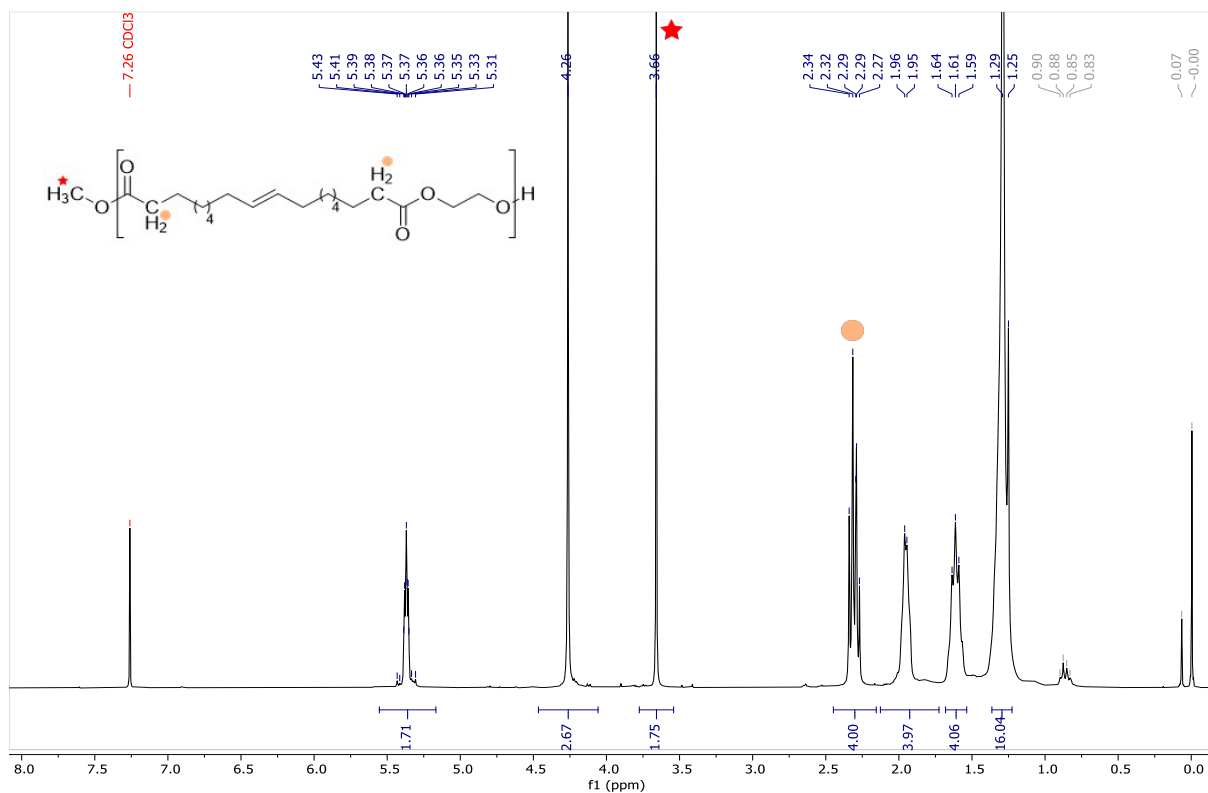


Figure S7. ¹H NMR spectrum of oligomer with ethylene glycol.

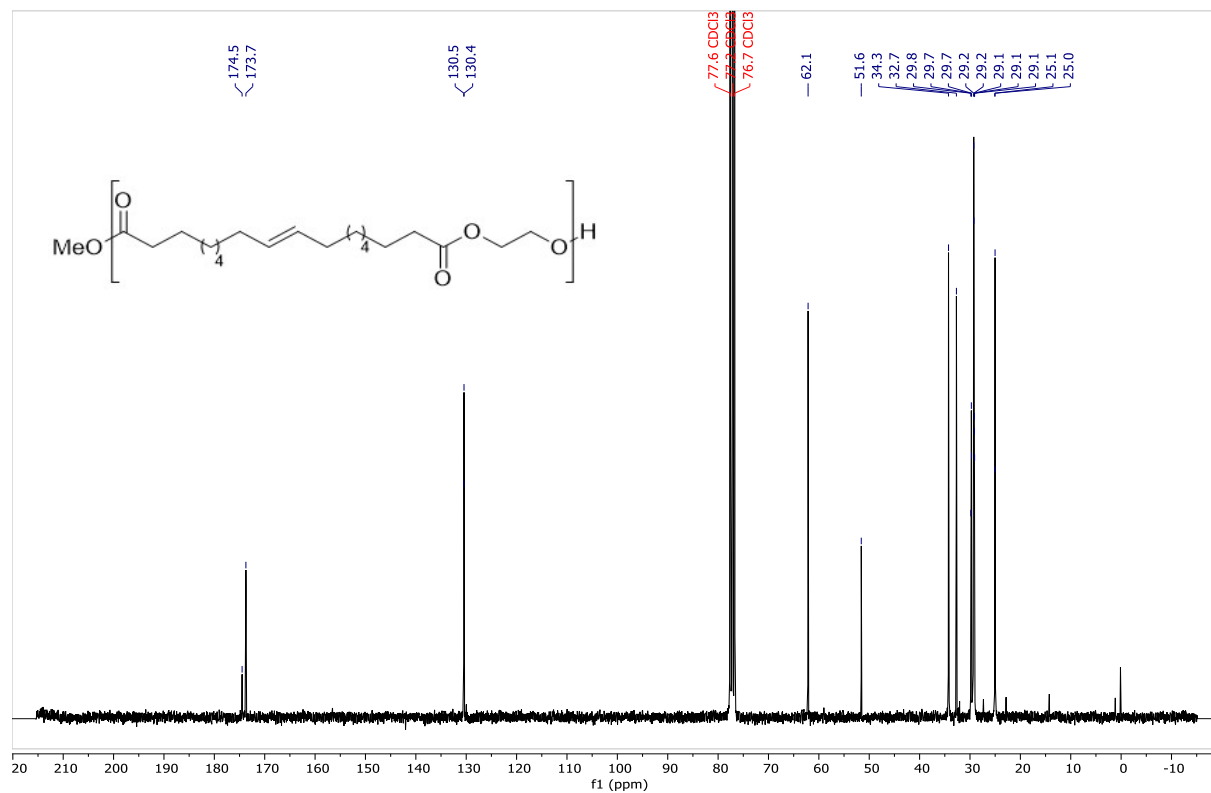


Figure S8. ¹³C NMR spectrum of oligomer with ethylene glycol.

4. 3. Oligomer with 1,4-butanediol (Table S2, Entry 3)

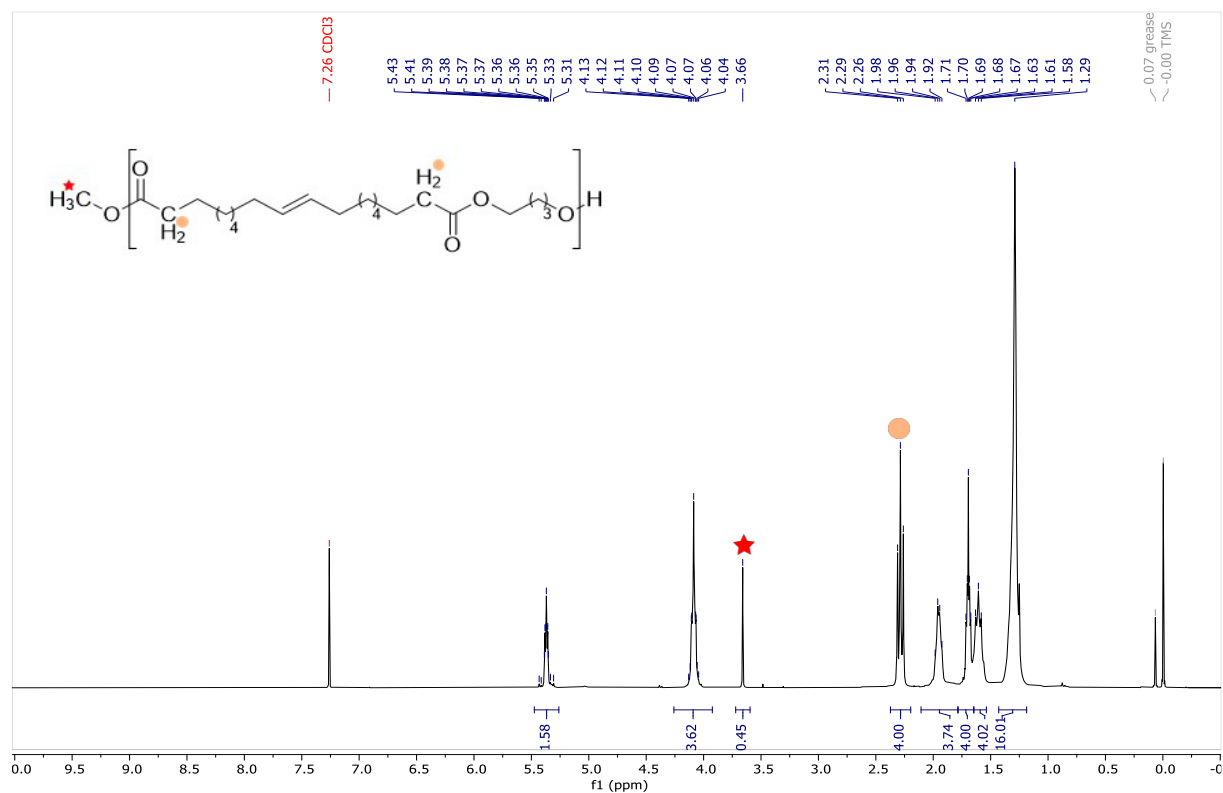


Figure S9. ¹H NMR spectrum of oligomer with 1,4-butanediol.

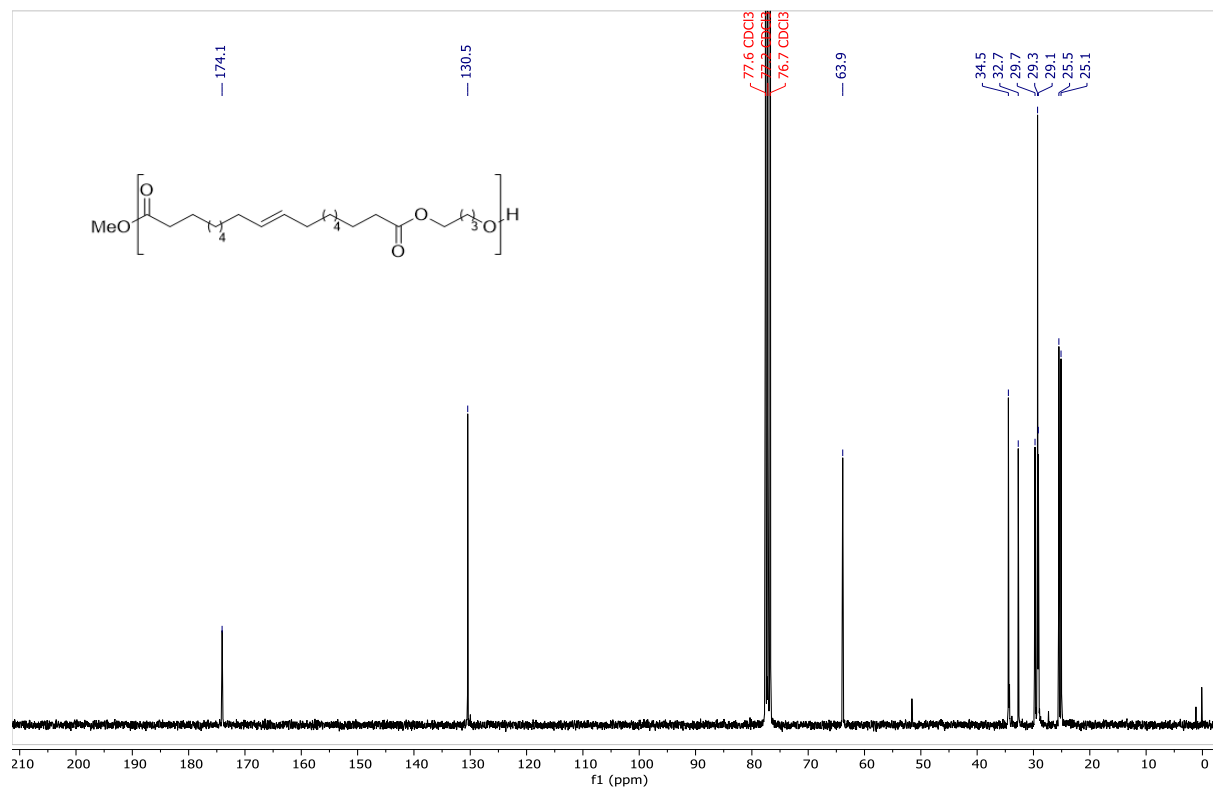


Figure S10. ¹³C NMR spectrum of oligomer with 1,4-butanediol.

4. 4. Oligomer with 1,6-hexanediol (Table S2, Entry 5)

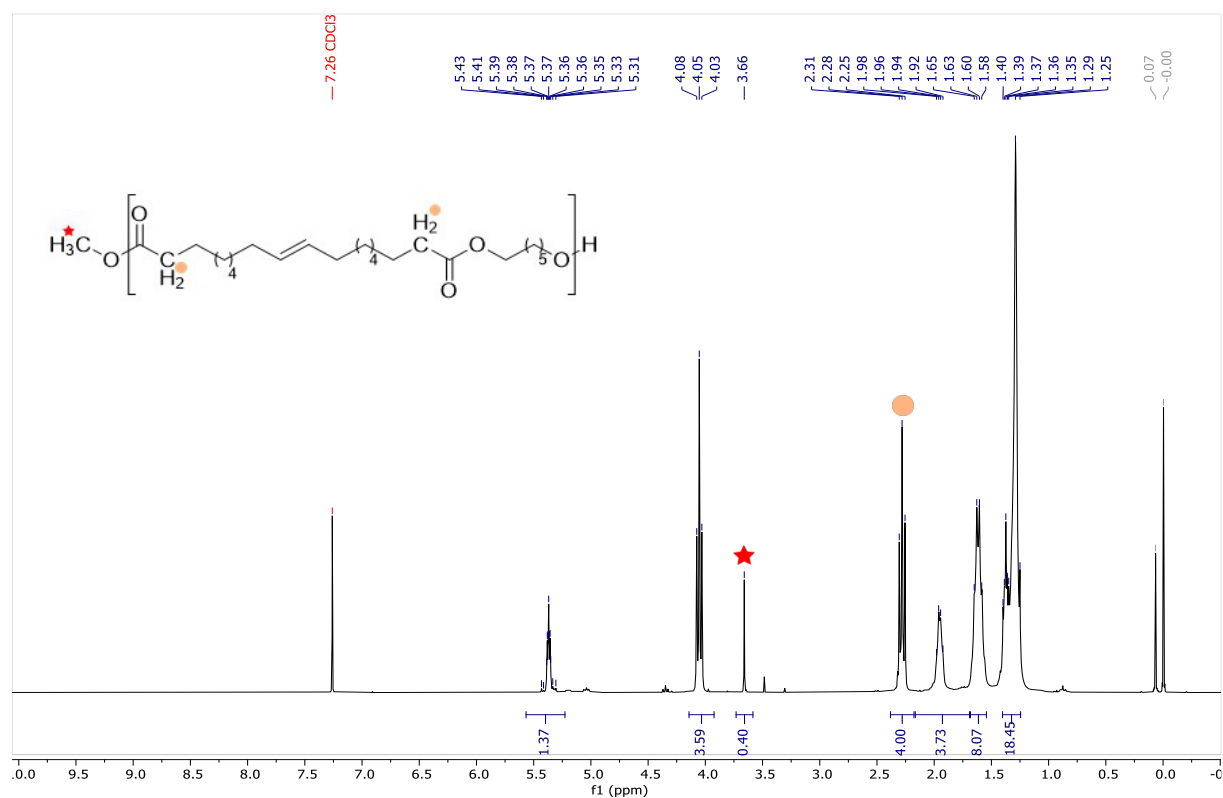


Figure S11. ¹H NMR spectrum of oligomer with 1,6-hexanediol.

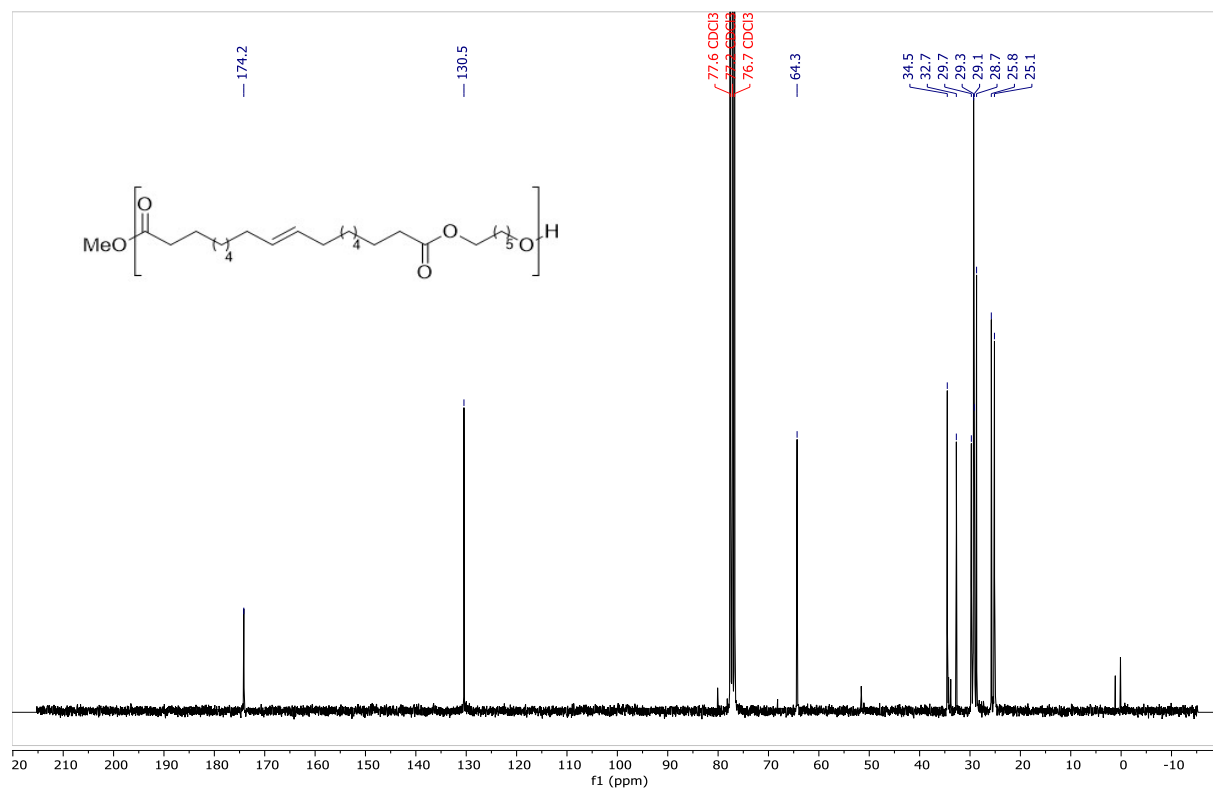
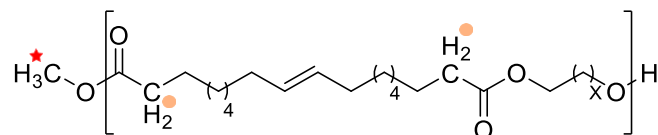


Figure S12. ¹³C NMR spectrum of oligomer with 1,6-hexanediol.

5. End group analysis

One method for figuring out a polymer's average molecular weight is end group analysis. The chemical environment for the end group in an NMR study differs from the environment for the repeat unit in the center of the oligomer chain. The acetyl group, which carries a methyl group with a chemical shift of roughly 3.7 ppm, will serve as the end groups. Each repeat unit of the chain has four aliphatic hydrogens that resonate between 2.2 and 2.4 ppm.

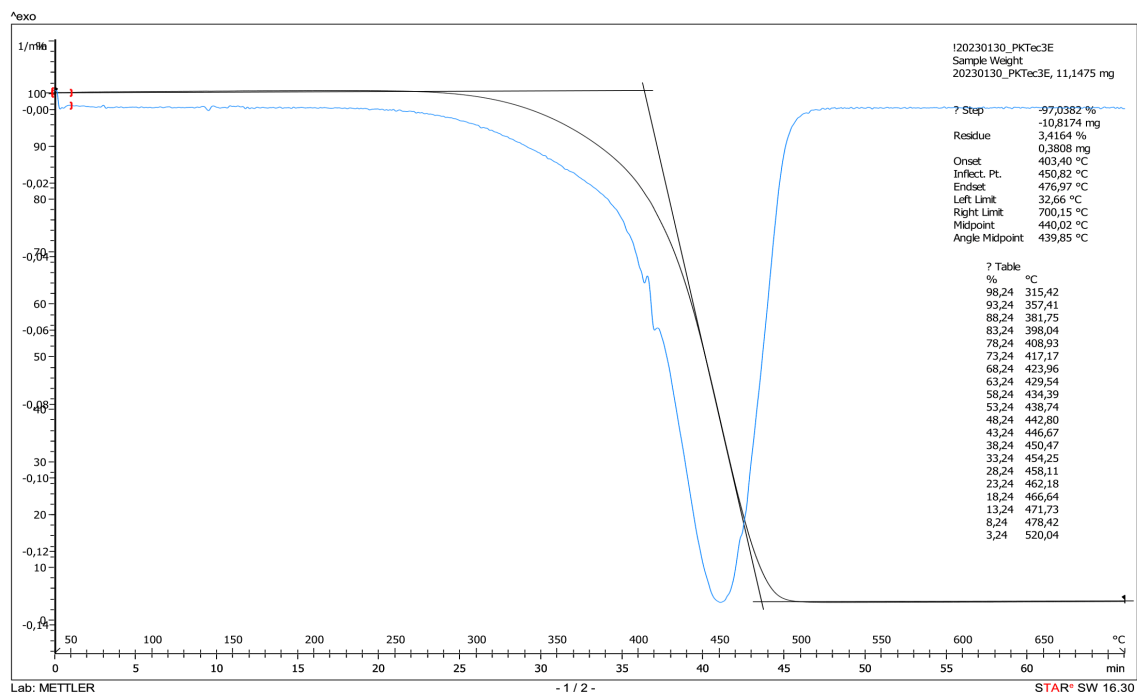


The number of repeat units (the degree of polymerization, DP) in the oligomer chain may be determined using the following equation, which involves measuring the integration of the methyl group hydrogens I_{end} by ^1H NMR and that of the methylene hydrogens (I_n) present in each repeat unit.

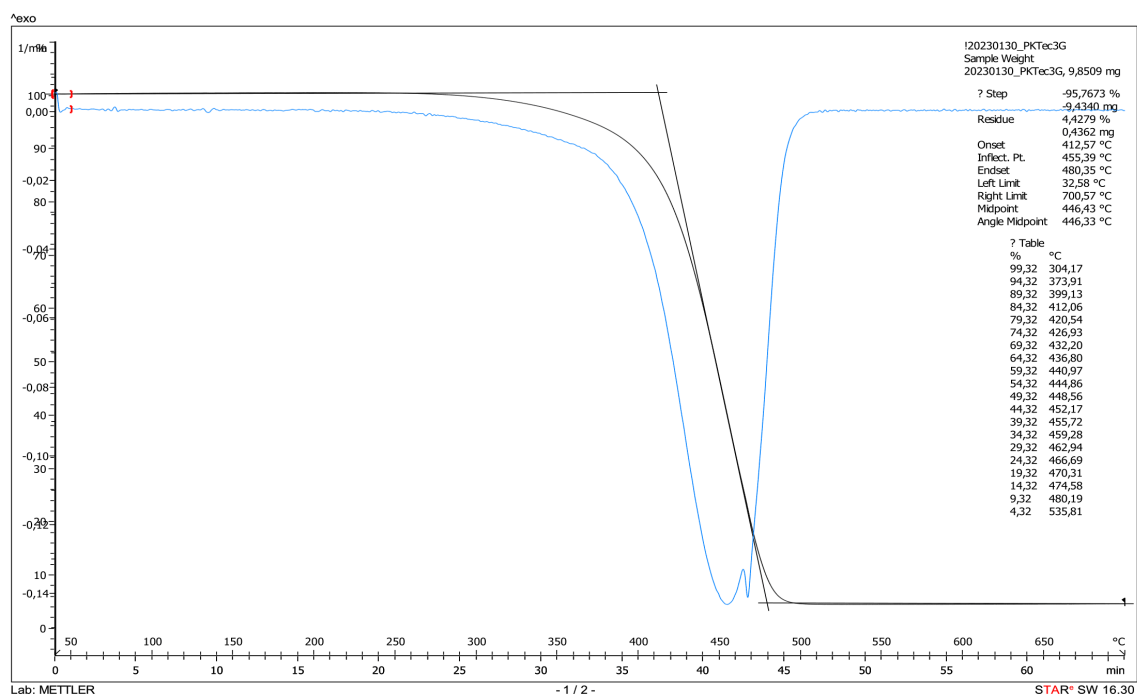
$$DP = \frac{I_{\text{end}}}{I_n} \cdot \frac{3}{4} \qquad M_n = RU \cdot DP$$

6. Thermogravimetric analysis

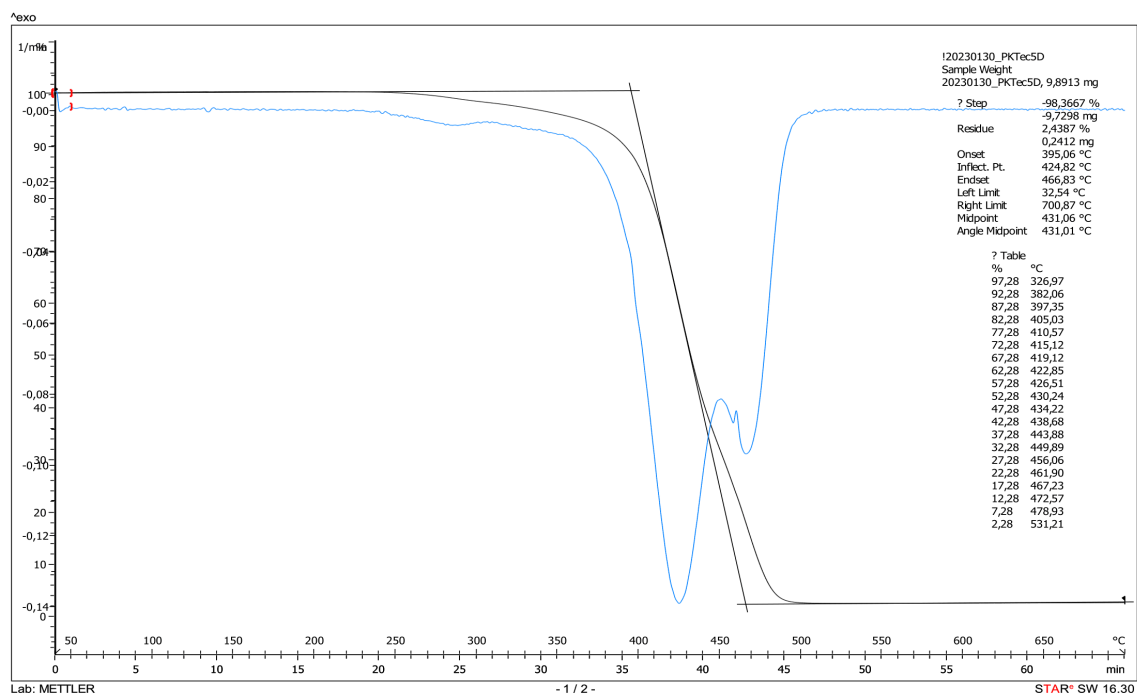
6. 1. Oligomer with ethylene glycol (Table S2, Entry 1)



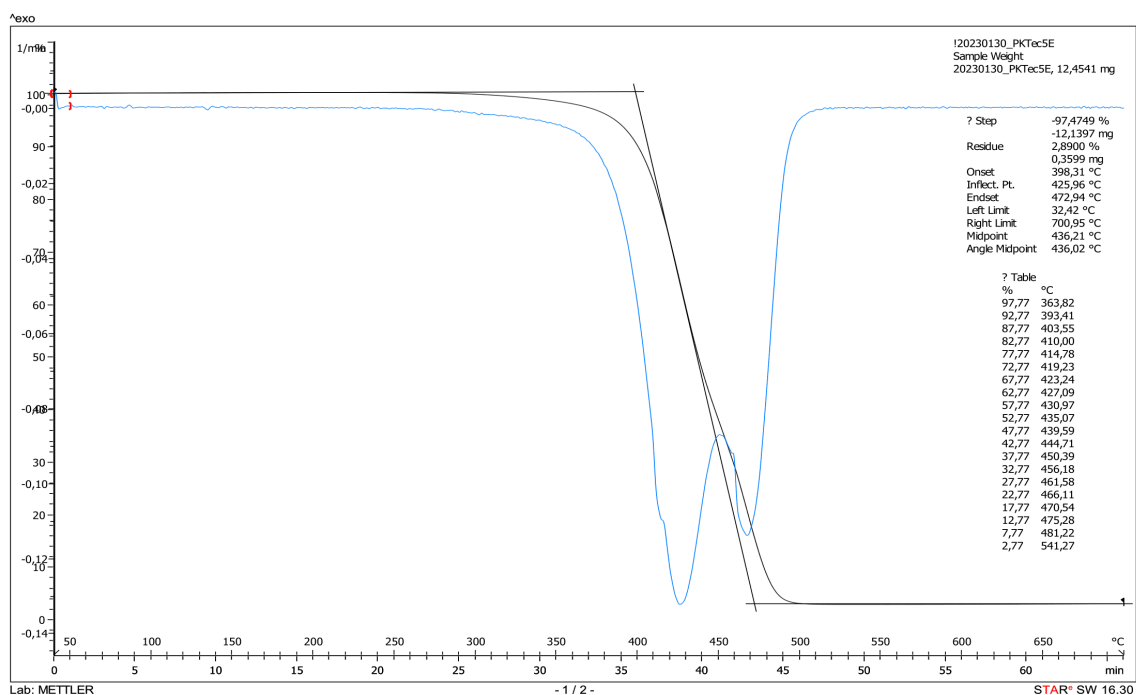
6. 2. Polymer with ethylene glycol (Table S2, Entry 2)



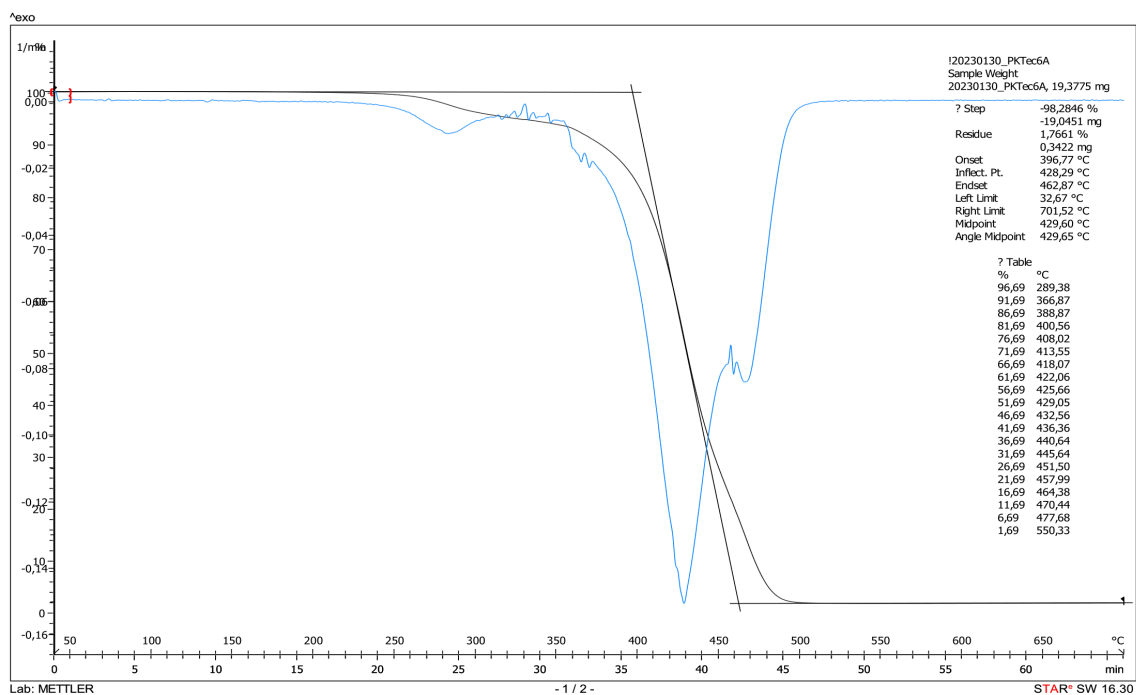
6. 3. Oligomer with 1,4-butanediol (Table S2, Entry 3)



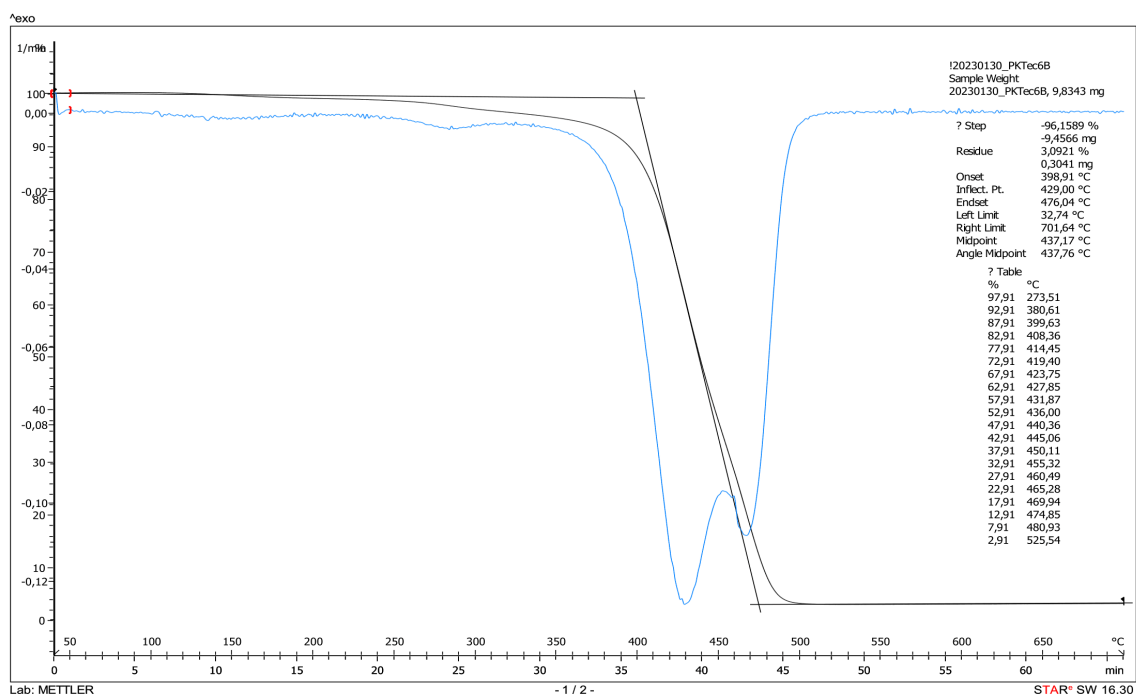
6. 4. Polymer with 1,4-butanediol (Table S2, Entry 4)



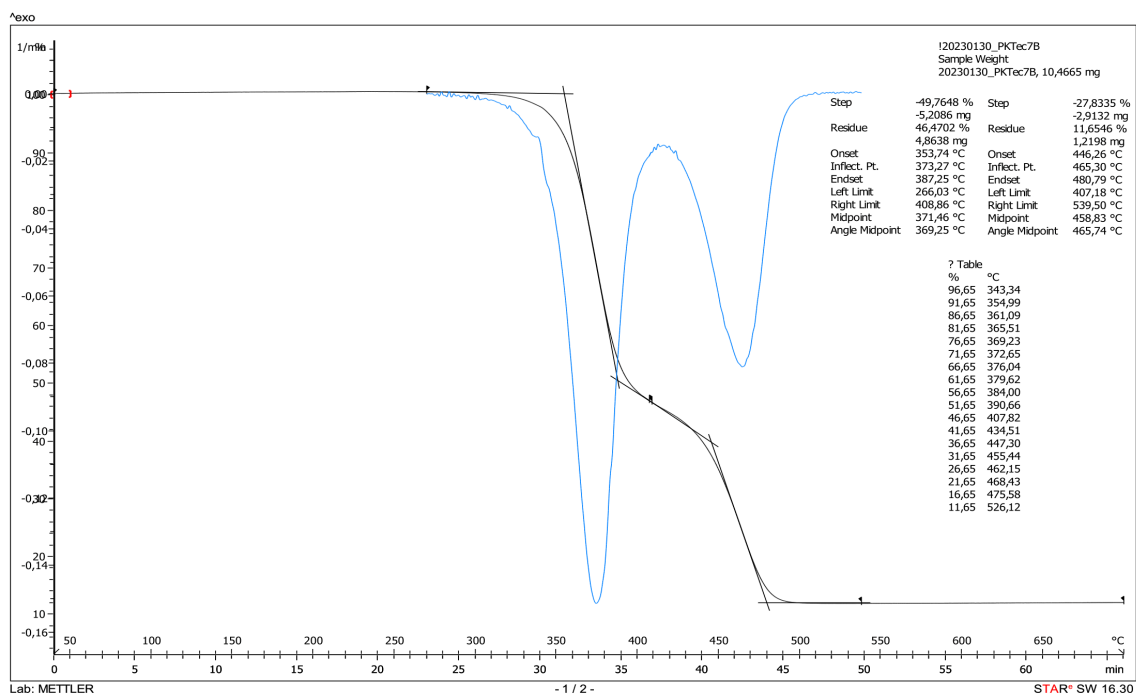
6. 5. Oligomer with 1,6-hexanediol (Table S2, Entry 5)



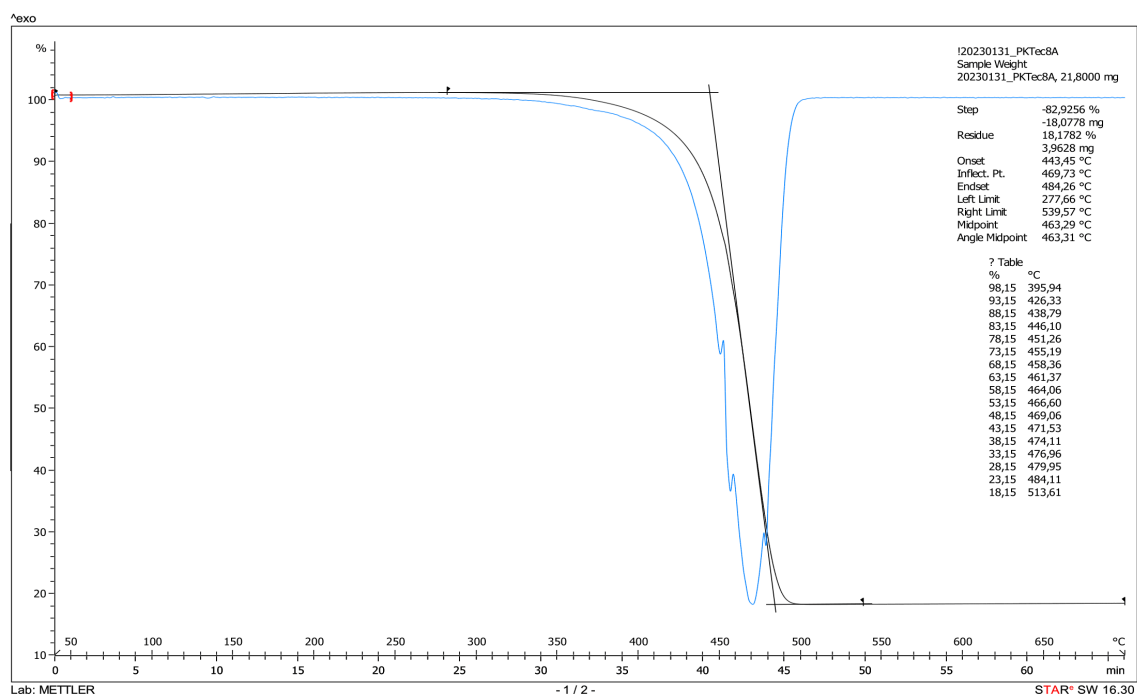
6. 6. Polymer with 1,6-hexanediol (Table S3, Entry 6)



6. 7. Polymer with 1,4-cyclohexanediol (Table S3, Entry 7)

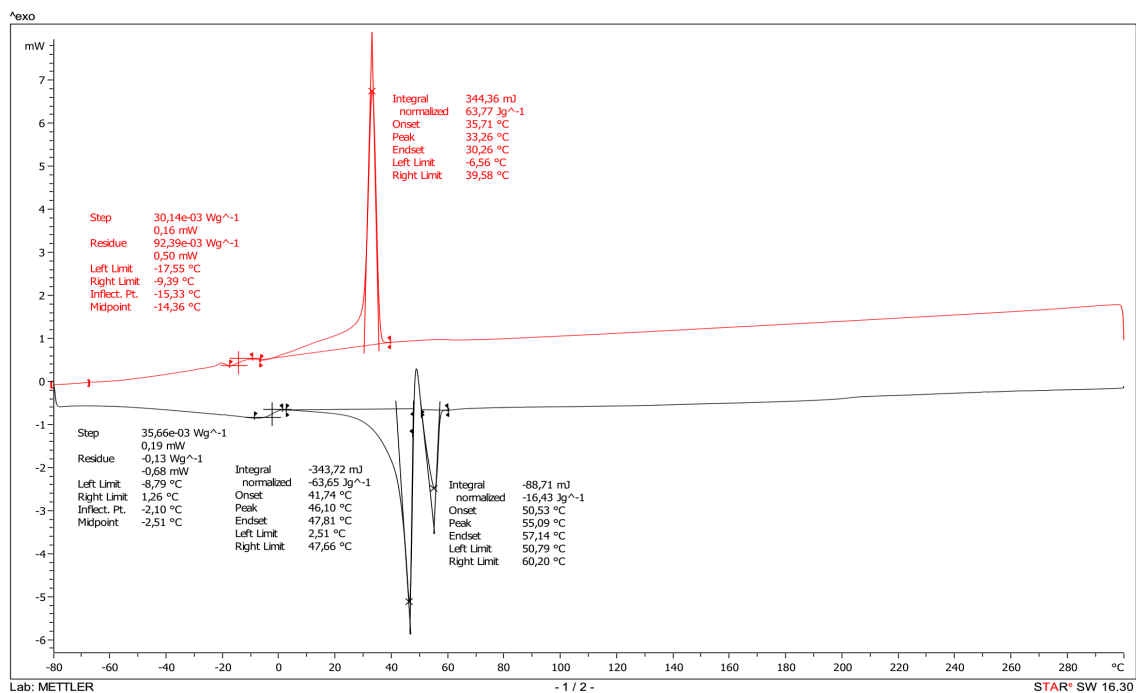


6. 8. Polymer with 1,8-diaminooctane (Table S3, Entry 8)

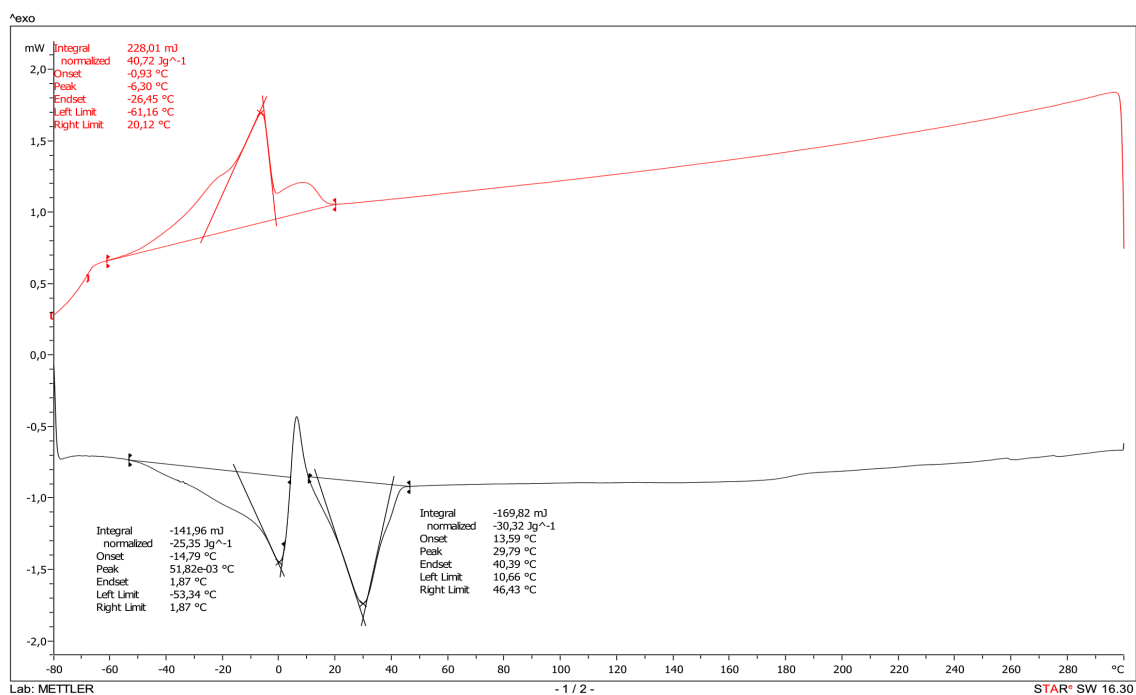


7. Differential Scanning Calorimetry

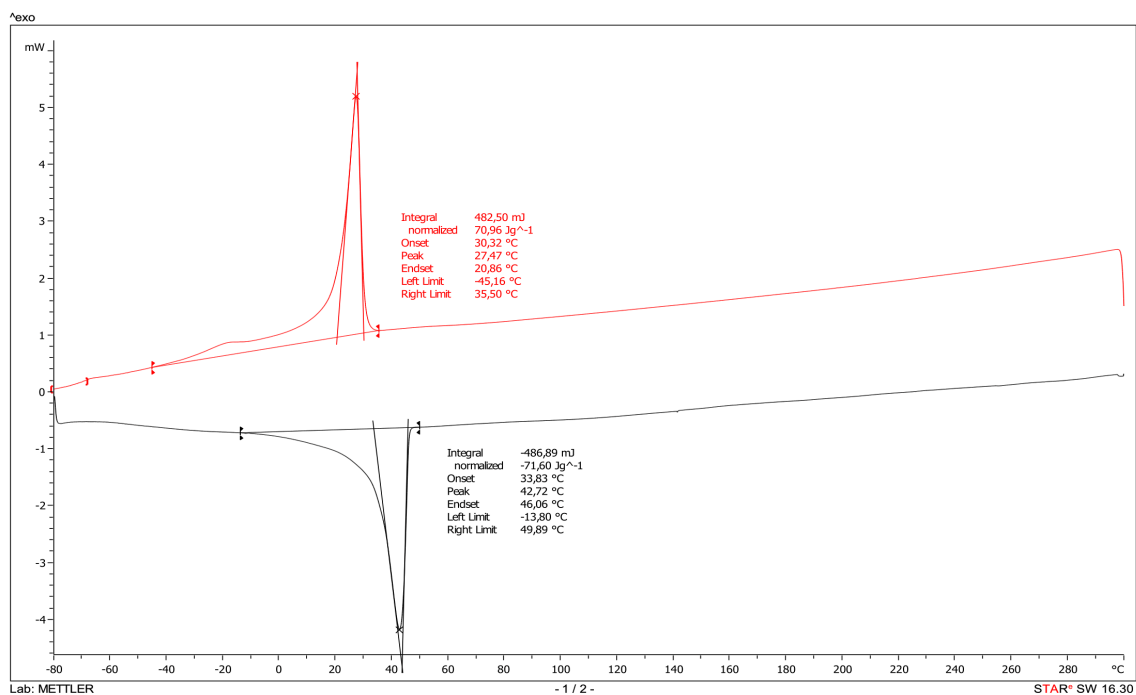
7. 1. Oligomer with ethylene glycol (Table S2, Entry 1)



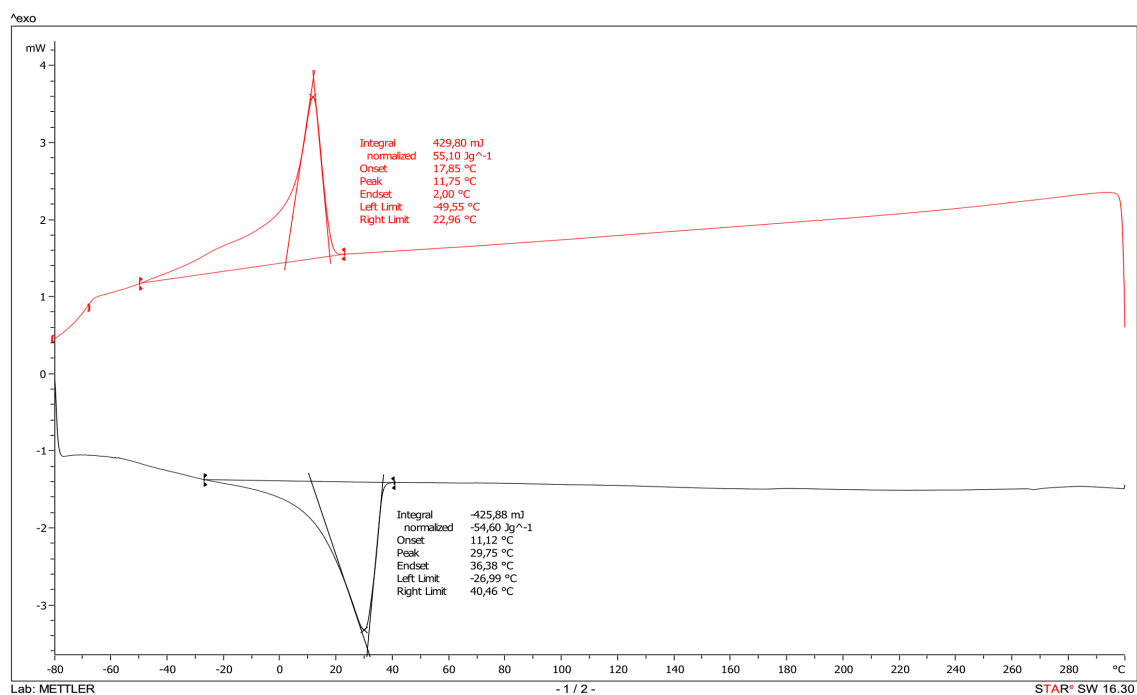
7. 2. Polymer with ethylene glycol (Table S2, Entry 2)



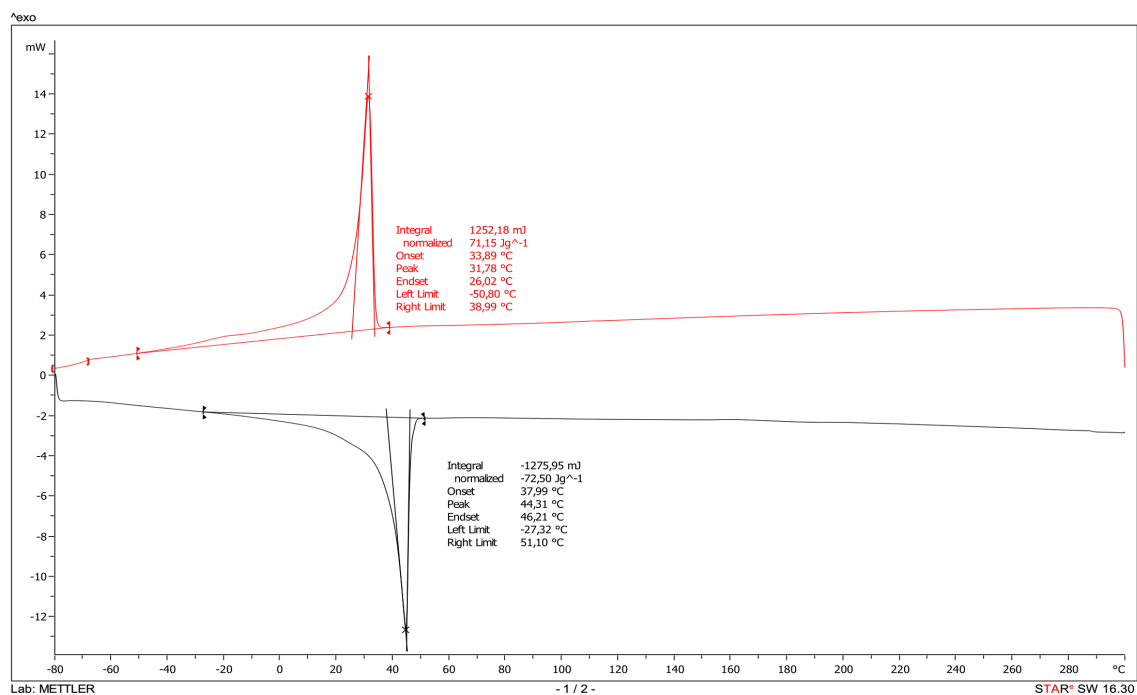
7. 3. Oligomer with 1,4-butanediol (Table S2, Entry 3)



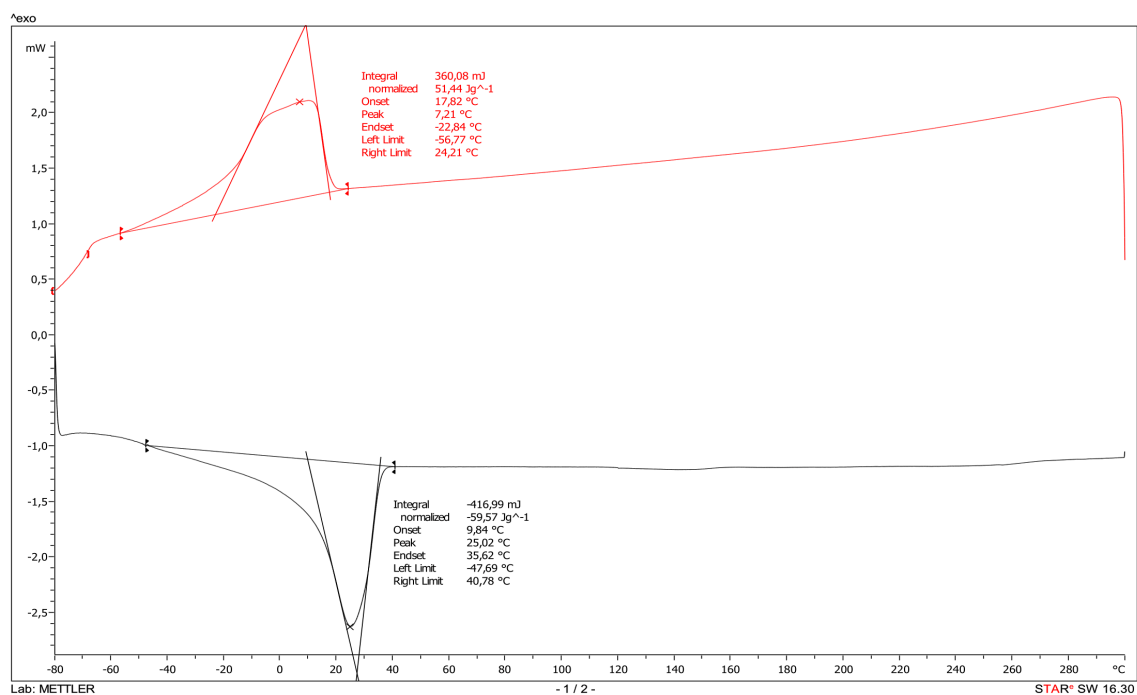
7. 4. Polymer with 1,4-butanediol (Table S2, Entry 4)



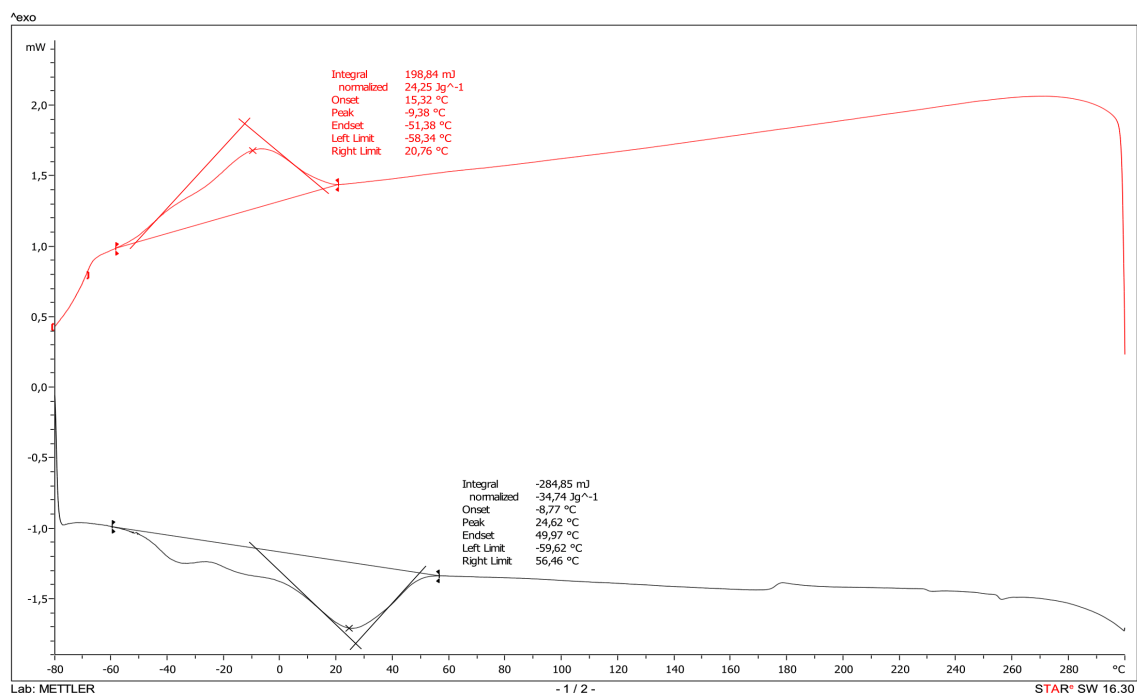
7. 5. Oligomer with 1,6-hexanediol (Table S2, Entry 5)



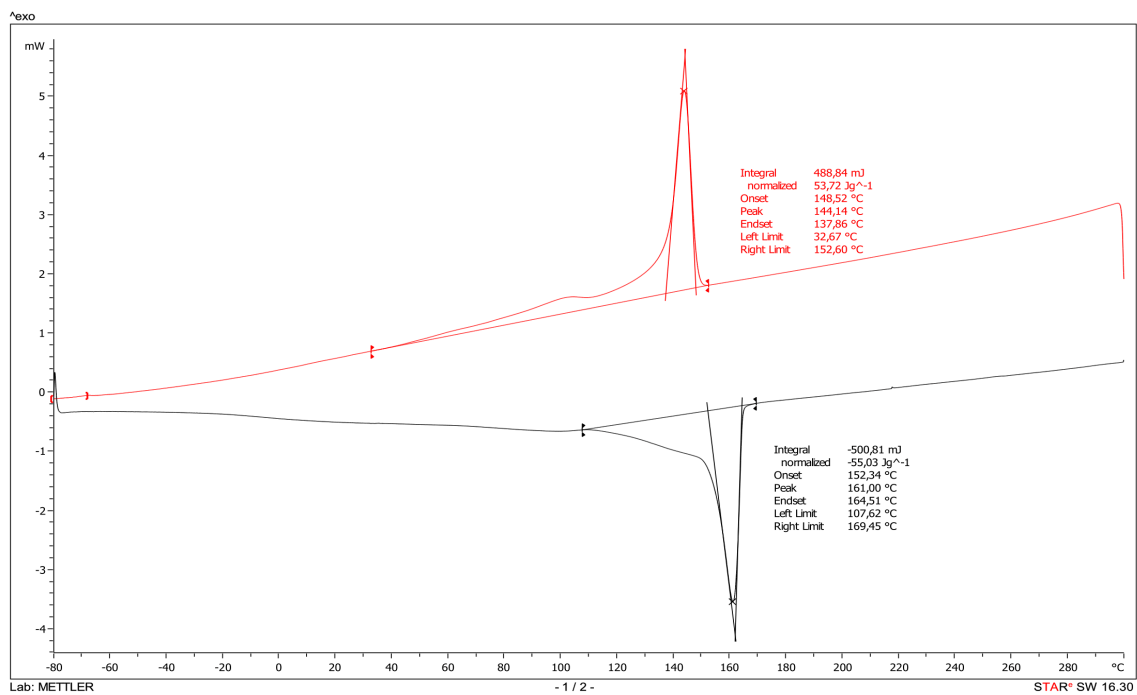
7. 6. Polymer with 1,6-hexanediol (Table S3, Entry 6)



7. 7. Polymer with 1,4-cyclohexanediol (Table S3, Entry 7)



7. 8. Polymer with 1,8-diaminooctane (Table S3, Entry 8)



8. References

- 1 G. Szczepaniak, K. Urbaniak, C. Wierzbicka, K. Kosiński, K. Skowerski and K. Grela, *ChemSusChem*, 2015, **8**, 4139–4148.
- 2 T. Witt, M. Häußler, S. Kulpa, S. Mecking and *Angew. Chem. Int. Ed. Engl.*, 2017, **56**, 7589–7594.