Supporting Information

Sustainable Terpene-Based Polyamides via Anionic Polymerization of a Pinene-Derived Lactam

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Materials and Methods

Chemicals were purchased from commercial supplies (Sigma-Aldrich or ABCR) and used as received unless otherwise noted. Flash chromatography (FC) was performed over silica gel of Acros (40-63 μm, Si 60). GPC/SEC measurements were performed on an Agilent 1200Series device equipped with a HFIP gel column and a UV detector. Hexafluoroisopropanol (HFIP) was used as the solvent, and the measurements were performed at 40 °C (continuous solvent flow of 0.5 mL/min). The internal pressure should not exceed 70 bar. Concentration of the polymer samples was 1 mg/mL, and the data evaluation was based on a calibration curve obtained from polymer standards of PSS. NMR measurements were conducted on Avance III (HD) NMR spectrometers from Bruker (^{1}H: 300 MHz; ^{13}C: 75 MHz).

MALDI-TOF MS spectra were recorded on a Bruker Ultra Flex TOF/TOF mass spectrometer with dithranol as the matrix, and samples were dissolved in formic acid (50 %) or HFIP before mixing with the matrix. Thermogravimetric analysis (TGA) was performed on a Q5000 SA from *TA Instruments* at a heating rate of 10 K/min under an inert gas atmosphere. DSC measurements were performed on a Q2000 device of *TA Instruments* at a heating and cooling rate of 10 K/min (for data interpretation, first heating cycle was omitted). Optical rotation was measured on a Perkin Elmer Polarimeter (Model 241 MC) at room temperature and λ = 589.3 nm (sodium D-line) at a concentration of 10 mg/mL in chloroform (monomers) or HFIP (polymers).

Synthesis of lactams 4 and Bz-4

Lactam **4** was synthesized starting from pinene (**1**) according to a procedure described previously by *Winnacker et al.*.[i]

^{1}H-NMR (300 MHz, Chloroform-*d*): δ [ppm] = 0.83 (s, 3 H), 1.27 (s, 3 H), 1.77 – 1.96 (m, 2 H), 2.00 (d, *J* = 12.8 Hz, 1 H), 2.16 (q, *J* = 6.4 Hz, 1 H), 2.53 – 2.72 (m, 2 H), 2.85 (ddd, *J* = 16.9 Hz, *J* = 8.5 Hz, *J* = 3.1 Hz, 1 H), 3.15 (t, *J* = 6.0 Hz, 1 H), 6.14 (s, 1 H).

^{13}C-NMR (75 MHz, Chloroform-*d*): δ [ppm] = 19.4, 22.9, 26.6, 27.8, 34.5, 41.6, 43.6, 57.8, 177.6.

For the synthesis of benzoylated lactam **Bz-4,** a modified procedure according to that described by Canham[ii] was applied: lactam **4** (0.9 g, 5.87 mmol, 1 eq.) was solved in THF (6 mL) and slowly added to a suspension of NaH (0.30 g, 60 wt% in oil, which was washed out prior to use) in THF (35 mL) at room temperature. After 1 h stirring, benzoyl chloride (1.07 g, 7.64 mmol, 1.3 eq.) was added slowly and the reaction solution was stirred for additional 14 h. After quenching with water (40 mL), the phases were separated and the aqueous phase was extracted with diethyl ether (3x50 mL). The combined organic phases were washed with saturated NaCl solution, dried over Na_2SO_4, filtered, and the solvent was removed at the rotavac. After purification via FC (hexane/ethyl acetate 20/1→ 5/1), the obtained solid was washed with water/pyridine (10/1) and recrystallized in pentane. **Bz-4** was obtained with 61% yield (0.89 g, 3.46 mmol).

DC: R_f = 0.44 (hexane/ ethyl acetate = 7/3) [UV]

^{1}H-NMR (300 MHz, chloroform-d): δ [ppm] = 0.90 (s, 3 H), 1.44 (s, 3 H), 1.88 – 2.15 (m, 2 H), 2.16 – 2.33 (m, 2 H), 2.72 (ddd, *J* = 14.8 Hz, *J* = 5.4 Hz, *J* = 2.3 Hz, 1 H), 2.82 (dt, J = 13.4 Hz, J = 7.5 Hz, 1 H), 3.22 (ddd, *J* = 14.8 Hz, *J* =11.7 Hz, *J* = 7.9 Hz, 1 H), 4.30 (ddd, *J* = 7.9 Hz, *J* = 4.0 Hz, *J* = 1.1 Hz, 1 H), 7.33–7. 71 (m, 5 H).

^{13}C-NMR (75 MHz, chloroform-*d*): δ [ppm] = 19.1, 23.9, 25.9, 28.2, 36.8, 41.4, 42.6, 61.0, 128.0, 128.3, 131.6, 136.4, 176.0, 178.1.

[a]$_D$ (10.0 mg/mL, chloroform) = –83.3.

CHN (%, $C_{16}H_{19}NO_2$): calculated: C: 74.68, H: 7.44, N: 5.44; found: C: 74.56, H: 7.51, N: 5.36.

Poly-4 via anionic polymerization of lactam 4

In a typical experiment, dried **4** (100 mg, 0.65 mmol), initatior (KO*t*Bu or NaH; ratio see tables) and coinitiator **Bz-4** (ratio see tables) were placed in a sealed vial under an inert gas atmosphere (glovebox, argon), which was then heated in a heating block. Afterwards the samples were cooled to rt and opened. HFIP was added until the product was solved, and the polymer was then precipitated via addition of hexane/ethyl acetate (3:1, 35 mL). The obtained suspension was centrifuged and decanted, and this cycle was repeated. After drying at 180 °C, pure **poly-4** was obtained. As an alternative, **poly-4** could be obtained by several washing steps, where the residue after the polymerization was washed with hexane/ethyl acetate several times in order to remove the remaining lactam monomer.

^{1}H-NMR (300 MHz, TFA-d): δ (ppm) = 0.93 (s, 3 H), 1.13 (s, 3 H), 1.58 – 1.94 (m, 4 H), 2.29 – 2.64 (m, 3 H), 4.05 (t, *J* = 8.5 Hz, 1 H), 7.51 (t, *J* = 7.6 Hz), 7.67 (d, *J* = 7.8 Hz).

^{13}C-NMR (TFA-d): δ [ppm] = 16.8, 28.5, 29.0, 30.3, 33.5, 40.8, 46.4, 55.3, 131.5, 180.9.

For the experiments without coinitiator **Bz-4**, the aromatic peak at 131.5 (from Bz) is missing as expected.

[a]$_D$ (10.0 mg/mL, HFIP) = +93.3.

Table S1. Further polymerizations of **4** to **poly-4**, exemplarily without **Bz-4** (entries 1-6) and with coinitiator **Bz-4** (entries 7-10) (details see main text).

Entry	Initiator(s)	Ratio	T	M_n/M_w	PDI	Yield
1	KO*t*Bu	50:1	150 °C	--	--	1
2	KO*t*Bu	50:1	250 °C	3400/7800	2.3	22
3	KO*t*Bu	25:1	250 °C	3200/9200	2.9	21
4	NaH	50:1	150 °C	--	--	1
5	NaH	50:1	250 °C	3200/8100	2.5	18
6	NaH	18:1	250 °C	4100/12500	3.0	44
7	KO*t*Bu / **Bz-4**	100:1 100:1	200 °C	--	--	2
8	KO*t*Bu / **Bz-4**	100:1 100:1	250 °C	--	--	2
9	NaH / **Bz-4**	70:1 100:1	200 °C	--	--	1
10	NaH / **Bz-4**	70:1 100:1	250 °C	--	--	2

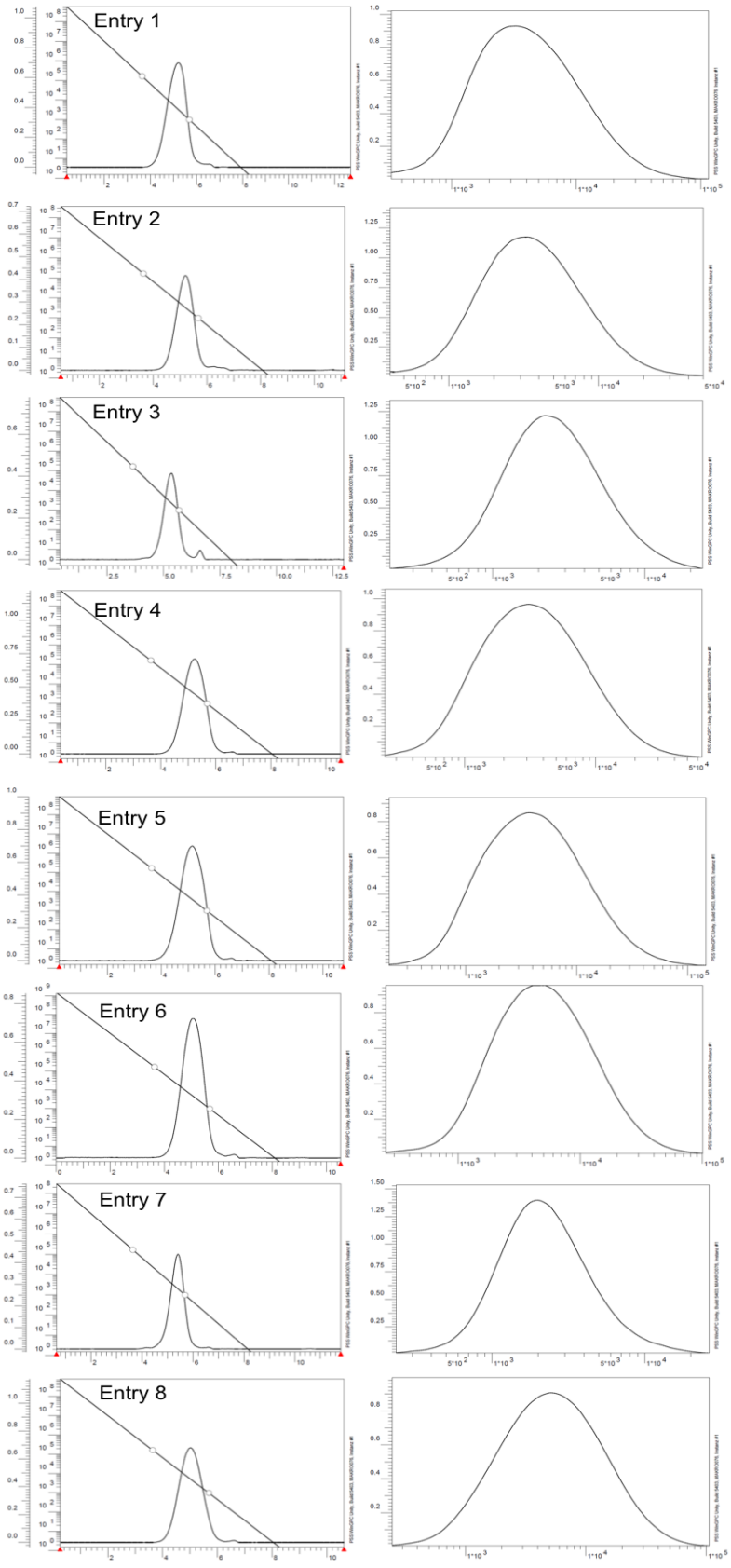

Figure S1. GPC/SEC elugrams (left) and mass distributions (right) of the polymerizations of table 1 (main text).

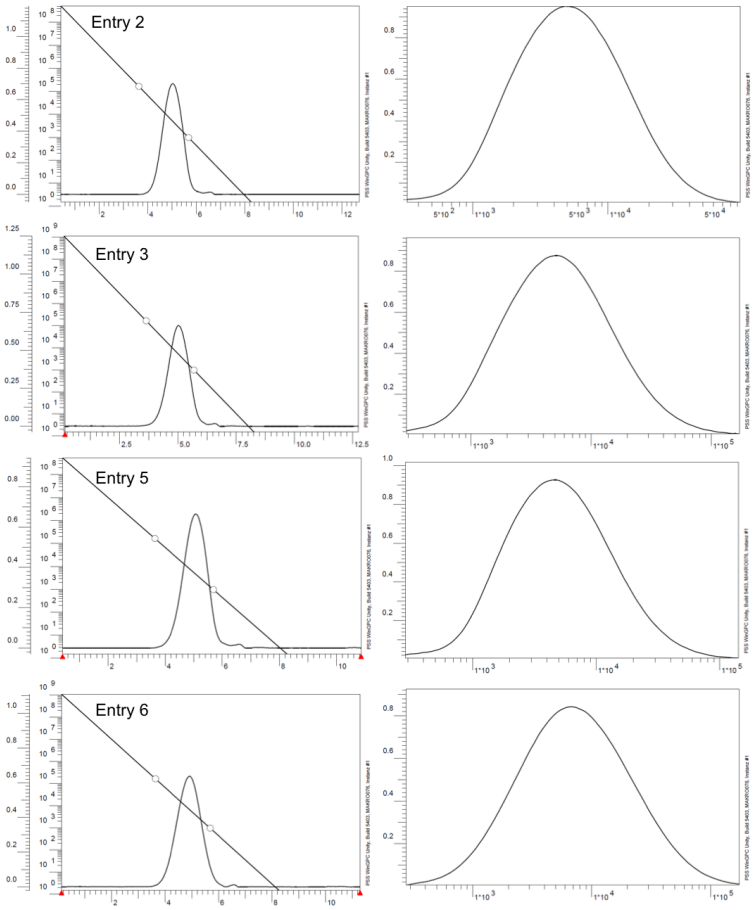

Figure S2. GPC/SEC elugrams and mass distributions of the polymerizations of table S1 (entries 2,3,5 and 6).

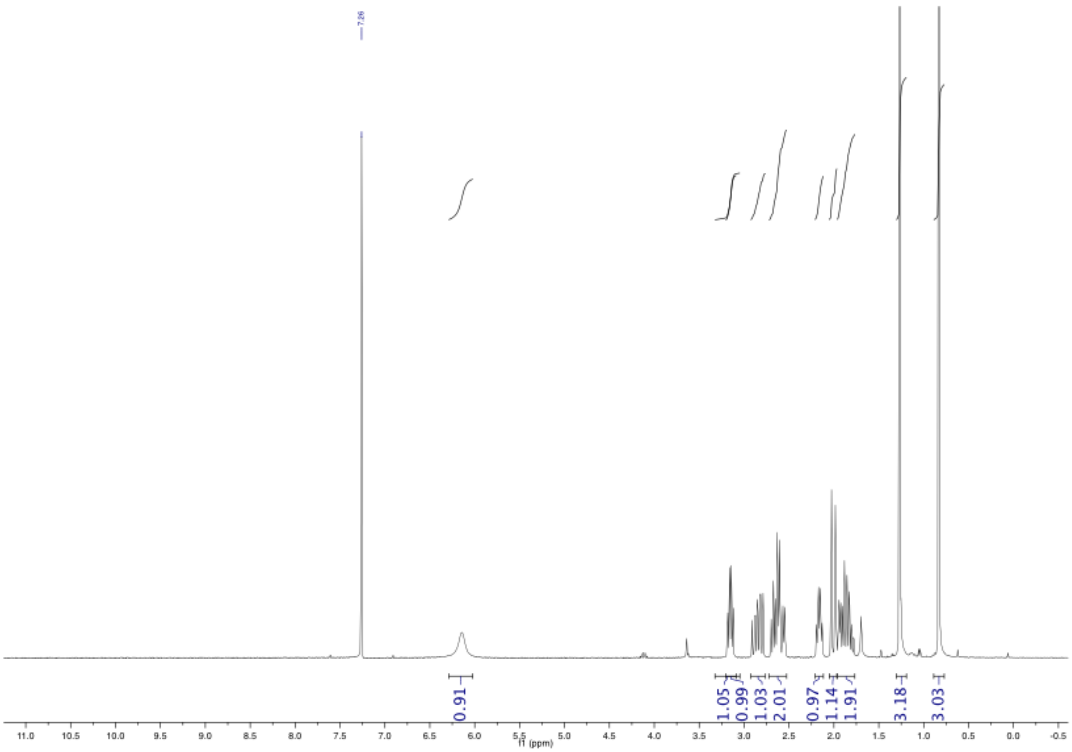

Figure S3. ^{1}H-NMR spectrum ($CDCl_3$) of lactam **4.**

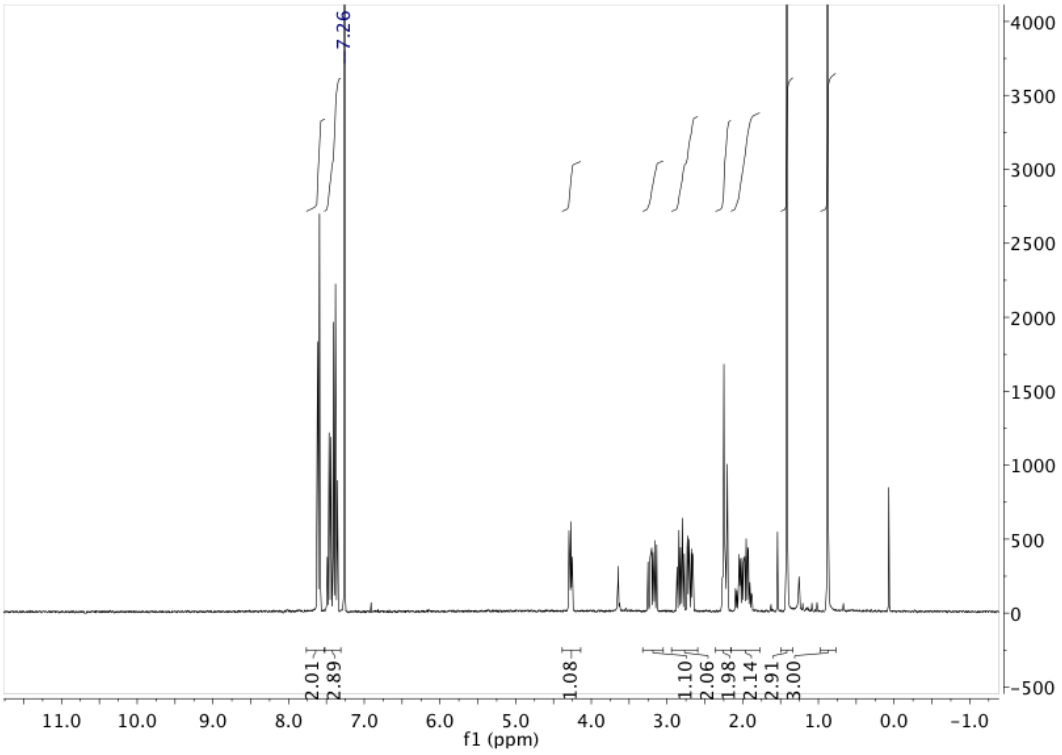

Figure S4. ^{1}H-NMR spectrum ($CDCl_3$) of lactam **Bz-4**.

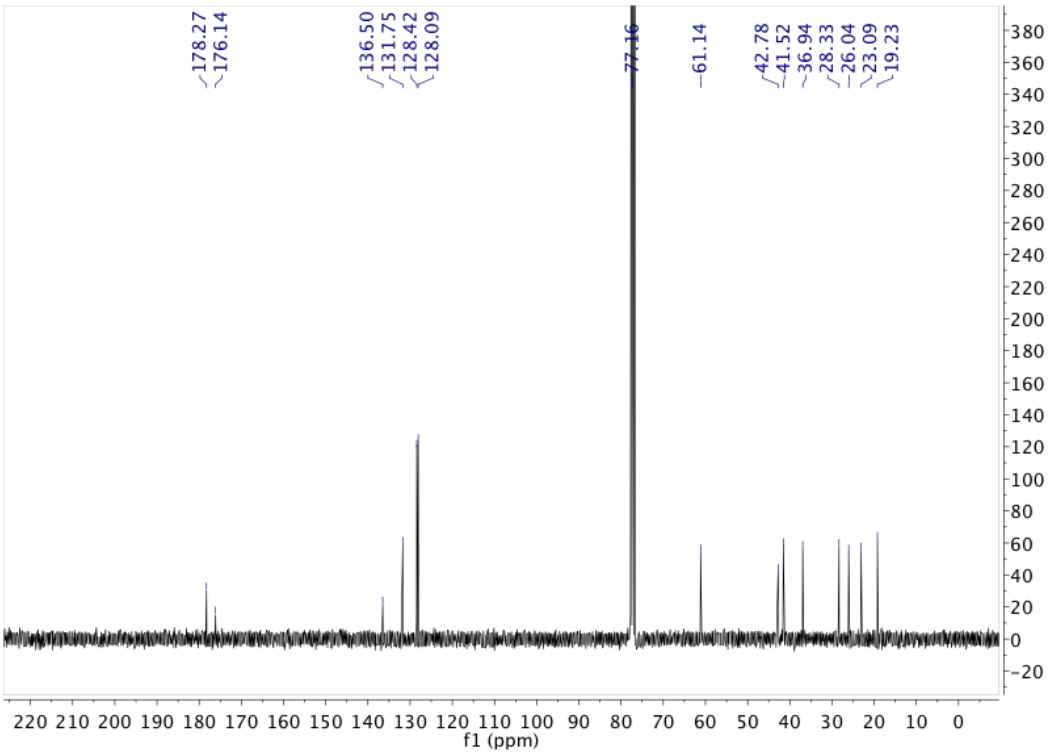

Figure S5. ^{13}C-NMR spectrum of lactam **Bz-4**.

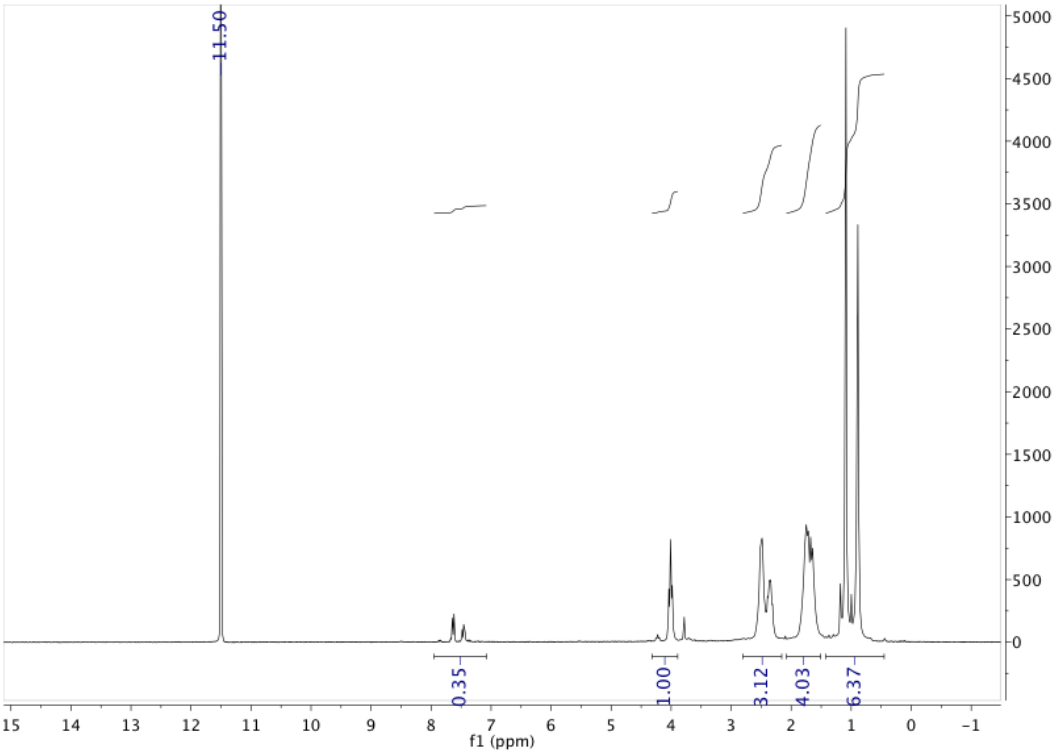

Figure S6. [1]H-NMR spectrum of **poly-4** (table 1, entry 1).

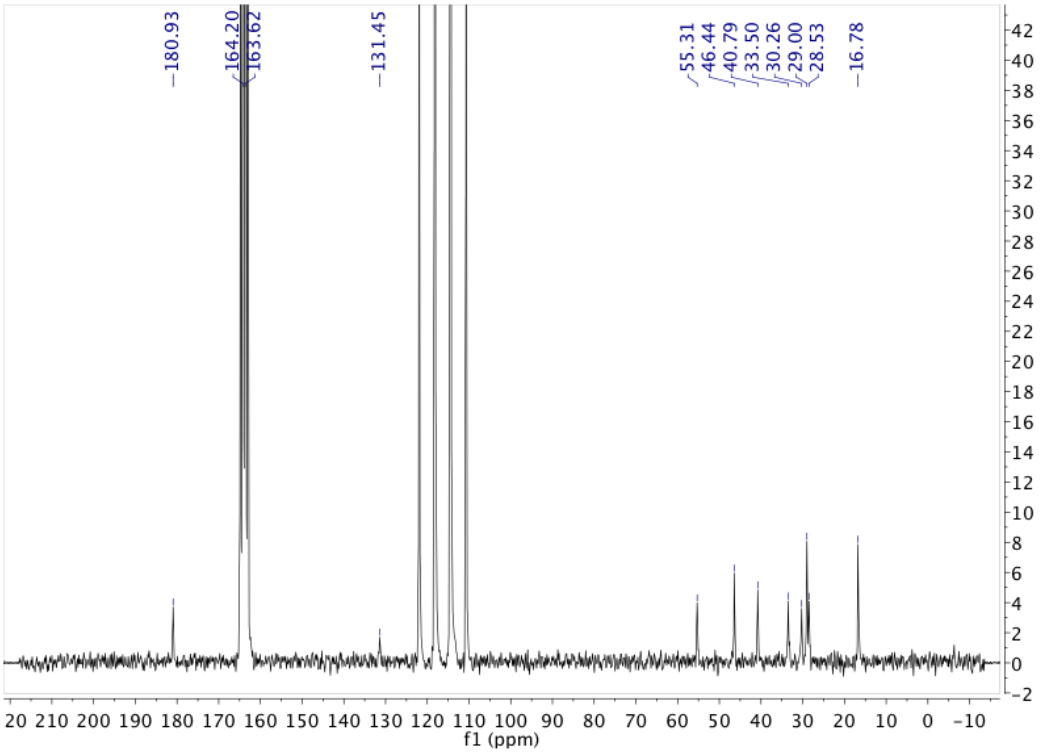

Figure S7. [13]C-NMR spectrum of **poly-4** (table 1, entry 1).

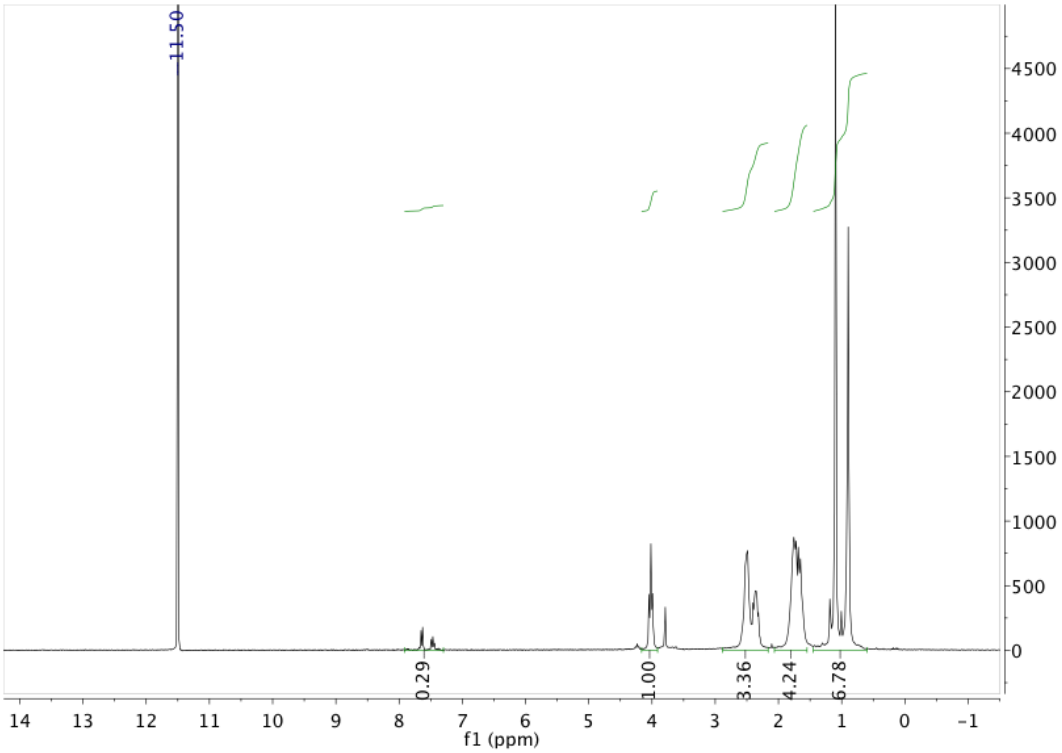

Figure S8. [1]H-NMR spectrum of **poly-4** (table 1, entry 4).

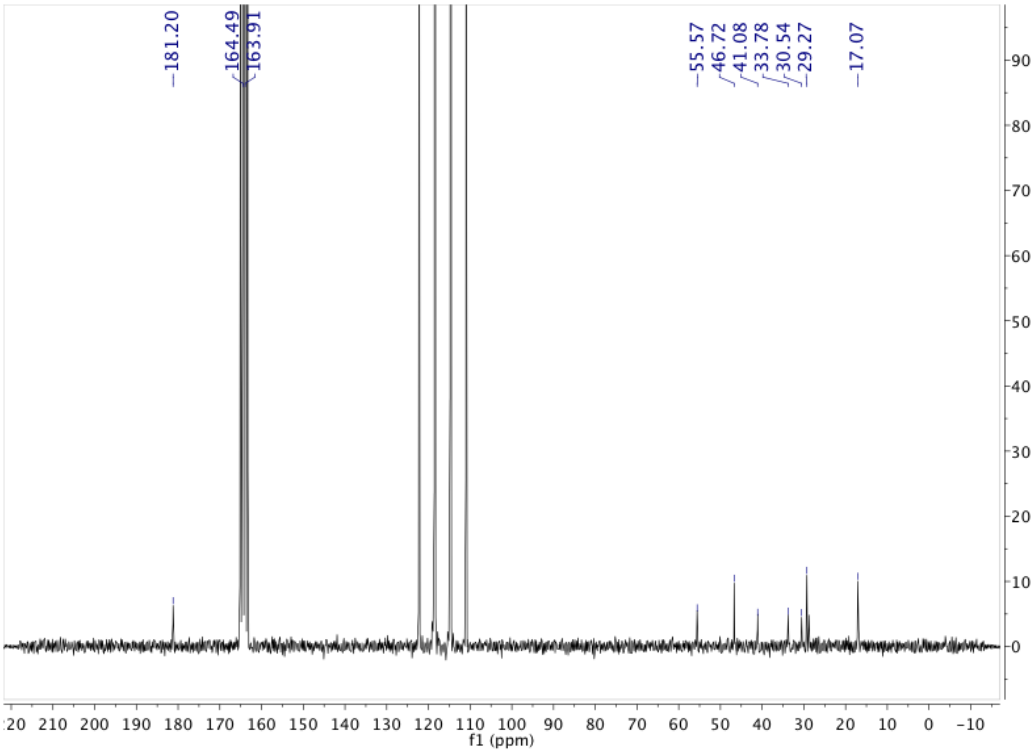

Figure S9. [13]C-NMR spectrum of **poly-4** (table 1, entry 4).

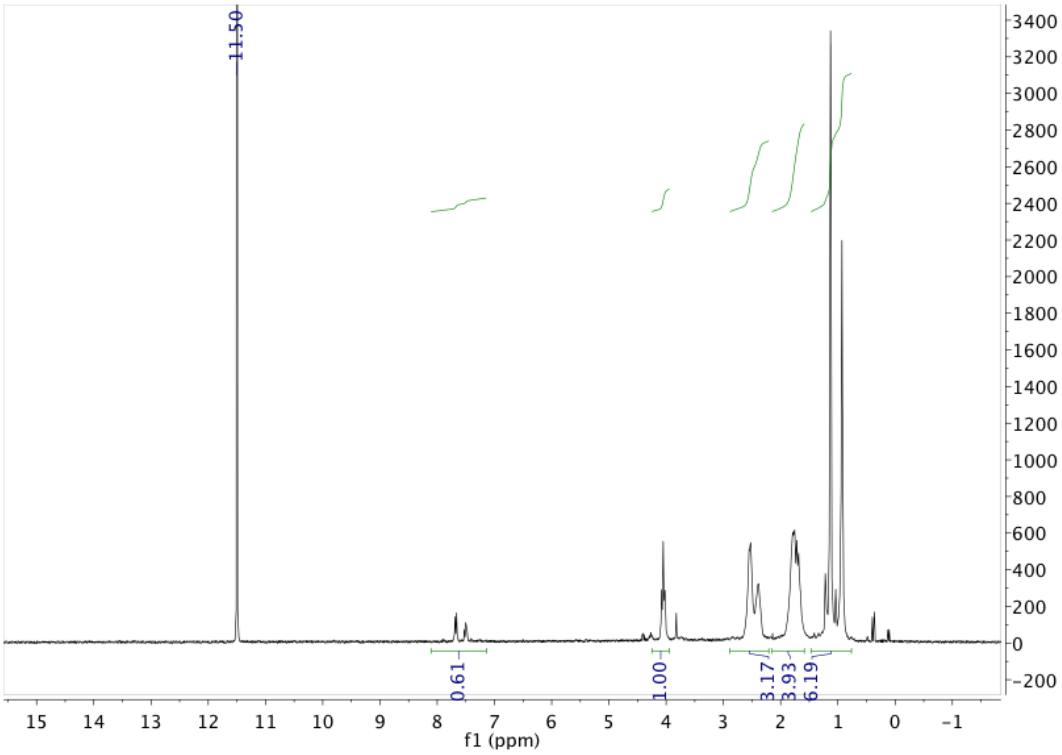

Figure S10. [1]H-NMR spectrum of **poly-4** (table 1, entry 5)

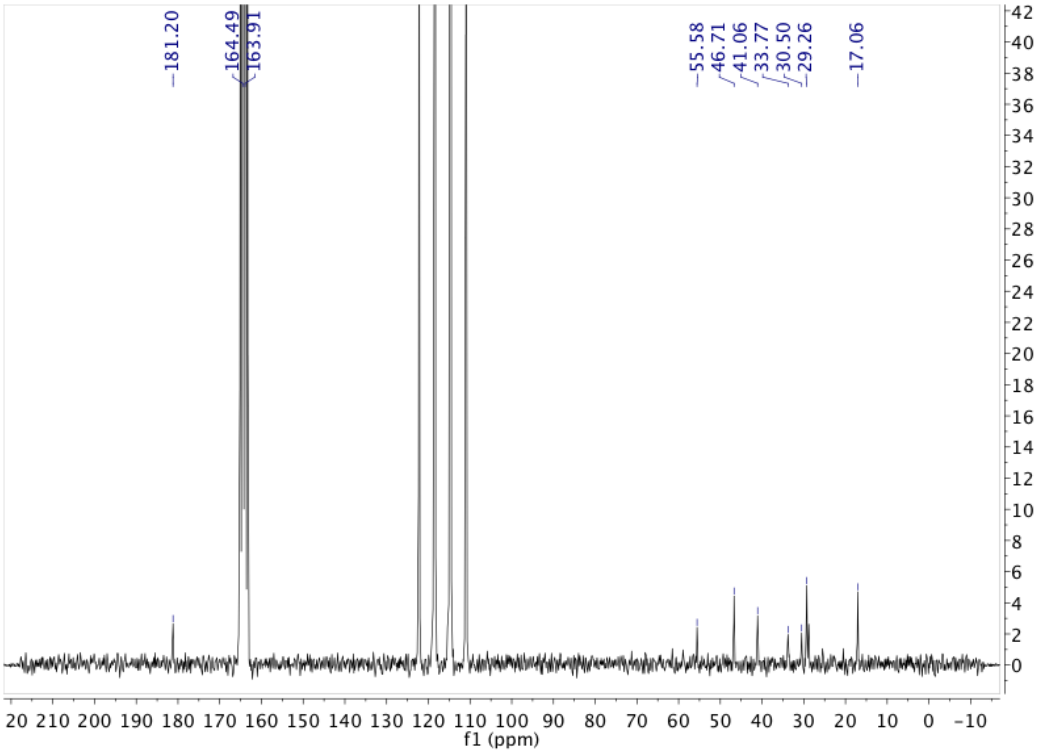

Figure S11.[13]CNMR spectrum of **poly-4** (table 1, entry 5).

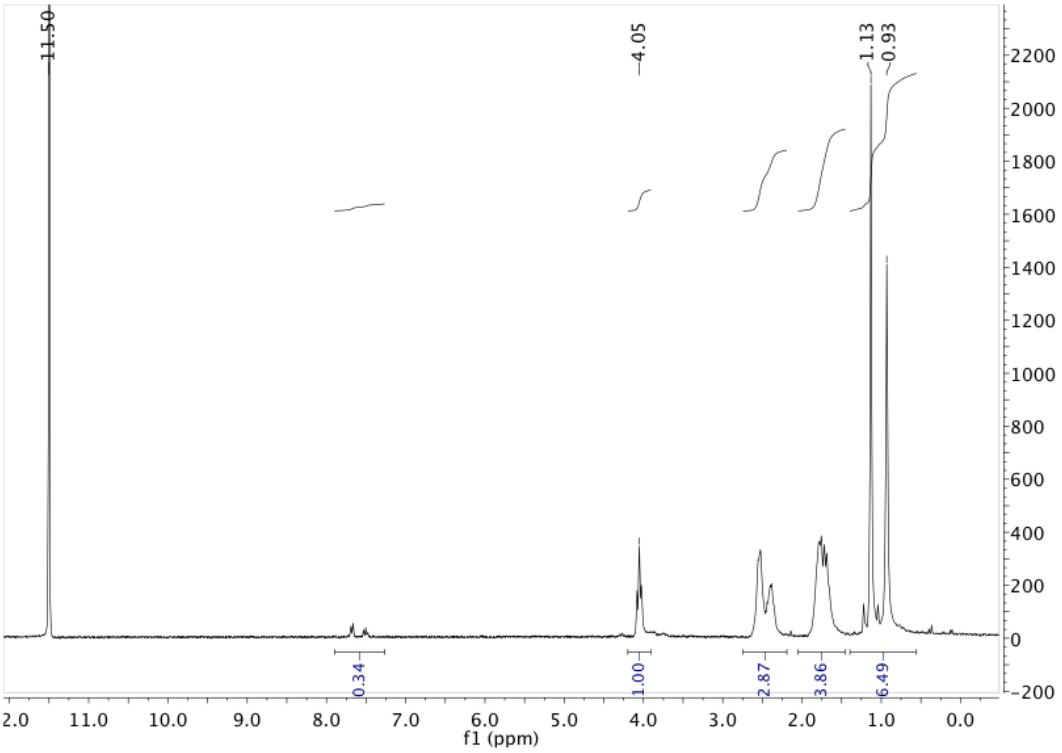

Figure S12. [1]H-NMR spectrum of **poly-4** (table 1, entry 6).

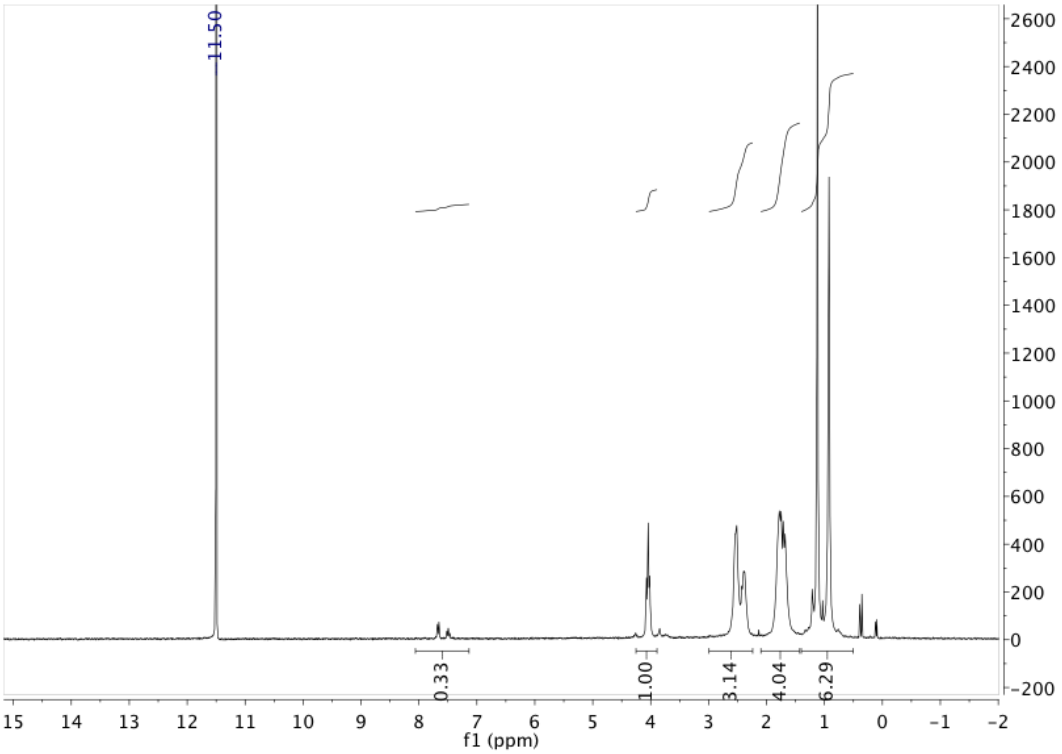

Figure S13. [1]H-NMR spectrum of **poly-4** (table 1, entry 8).

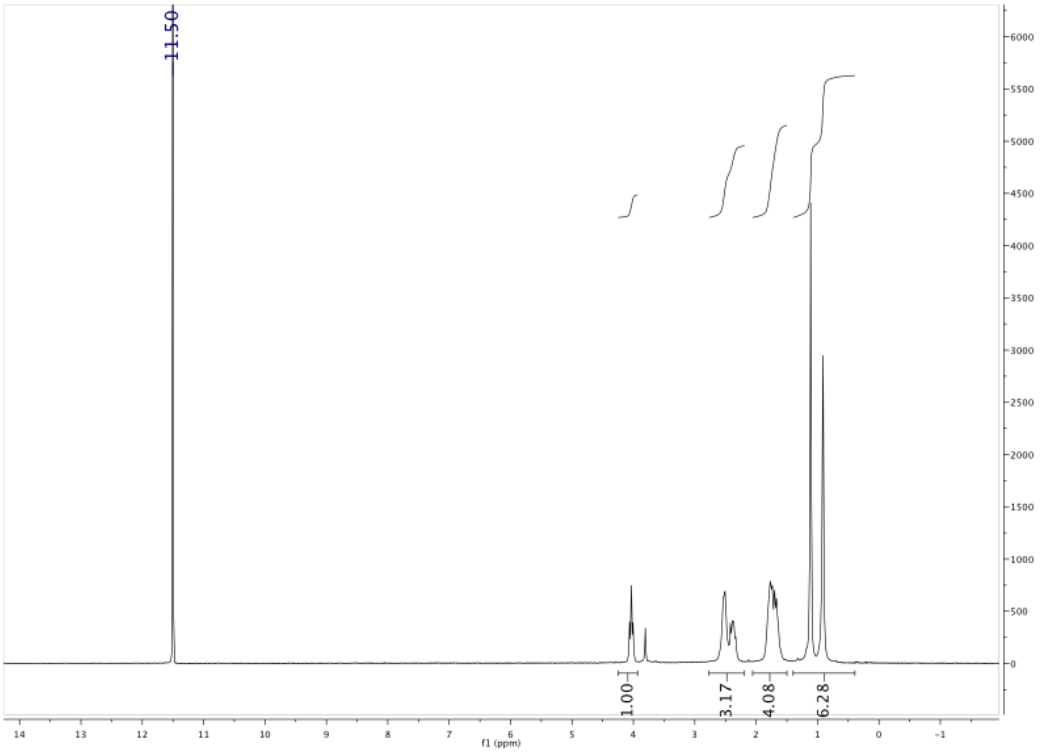

Figure S14. ^{1}H-NMR spectrum of **poly-4** (table S1, entry 2).

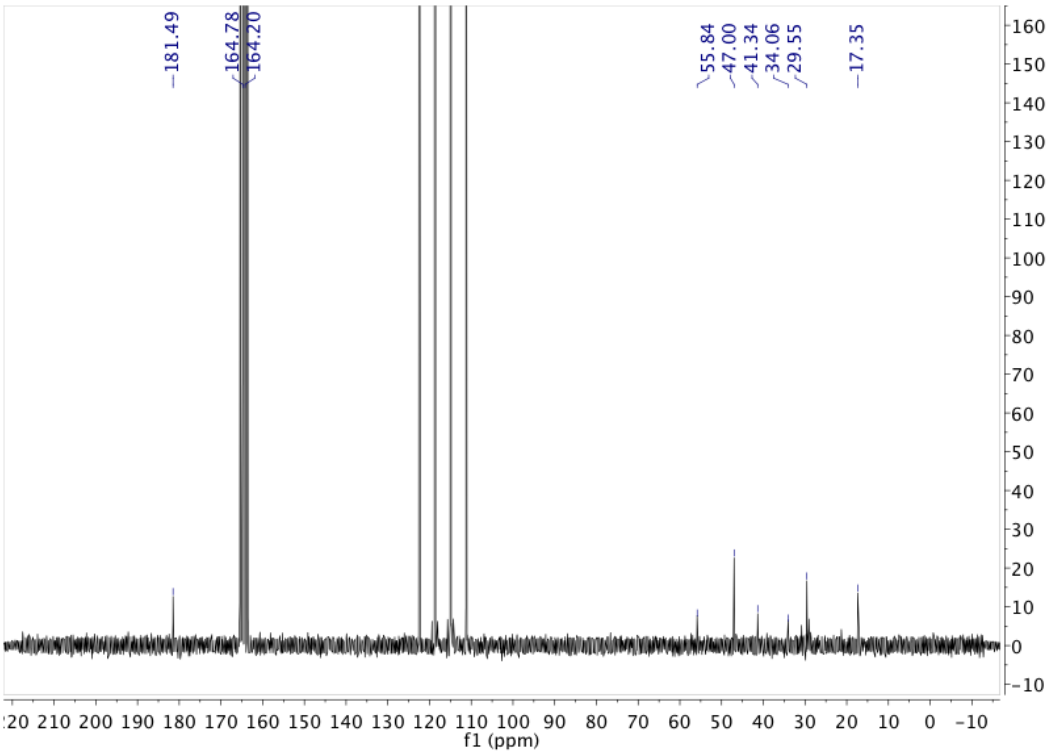

Figure S15. ^{13}C-NMR spectrum of **poly-4** (table S1, entry 2).

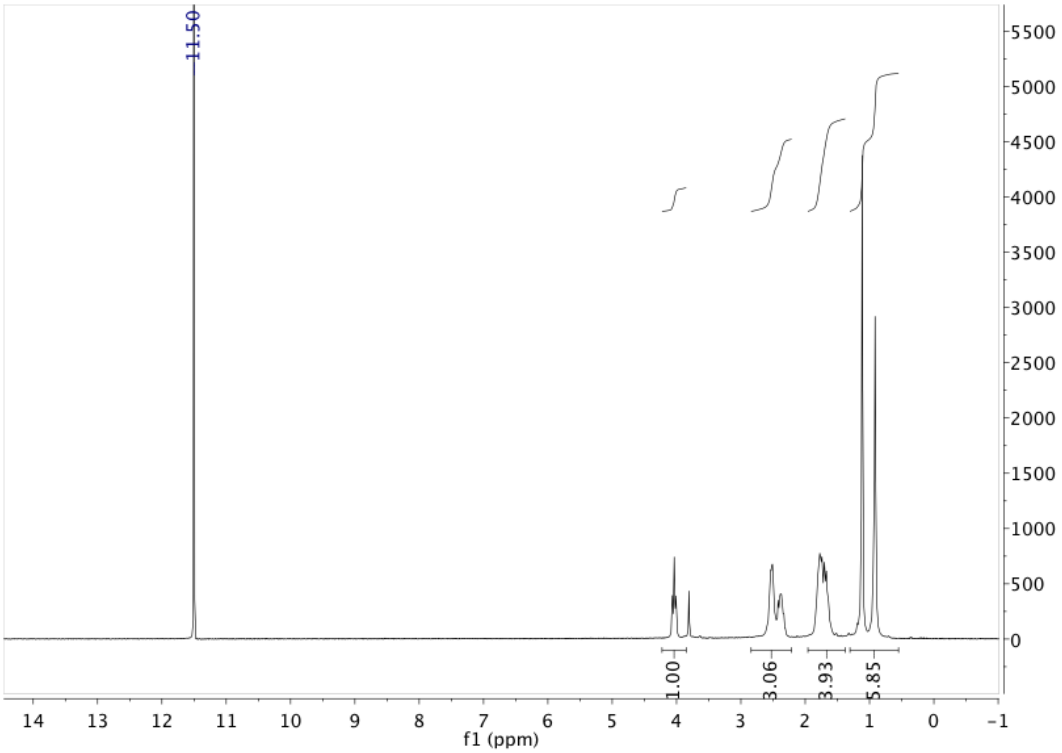

Figure S16. [1]H-NMR spectrum of **poly-4** (table S1, entry 5).

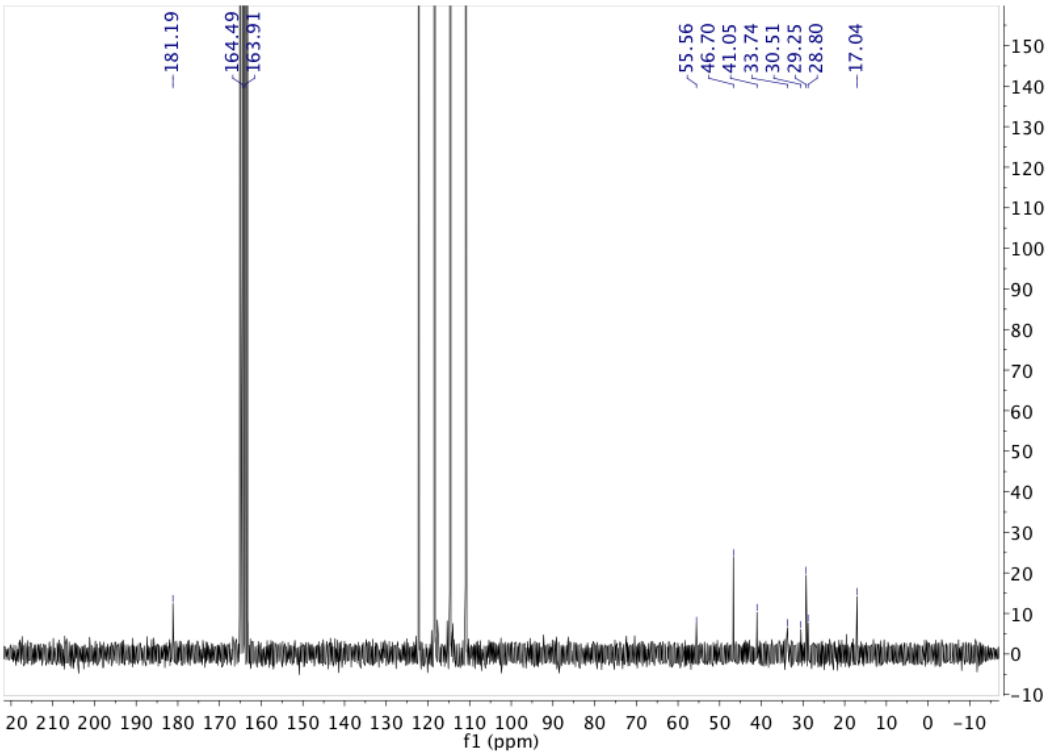

Figure S17. [13]C-NMR spectrum of **poly-4** (table S1, entry 5).

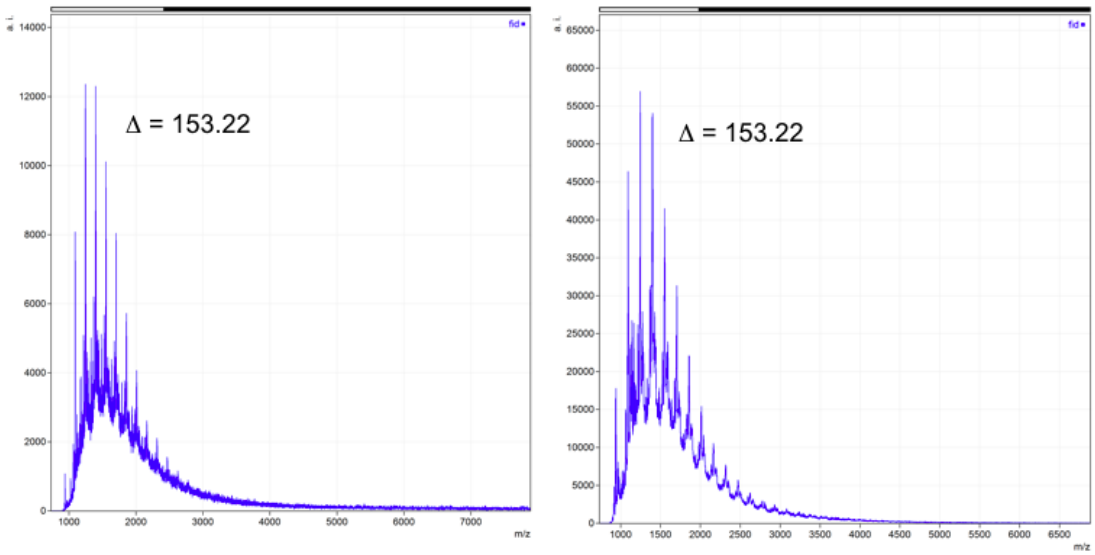

Figure S18. MALDI-MS spectra of two selected **poly-4** samples.

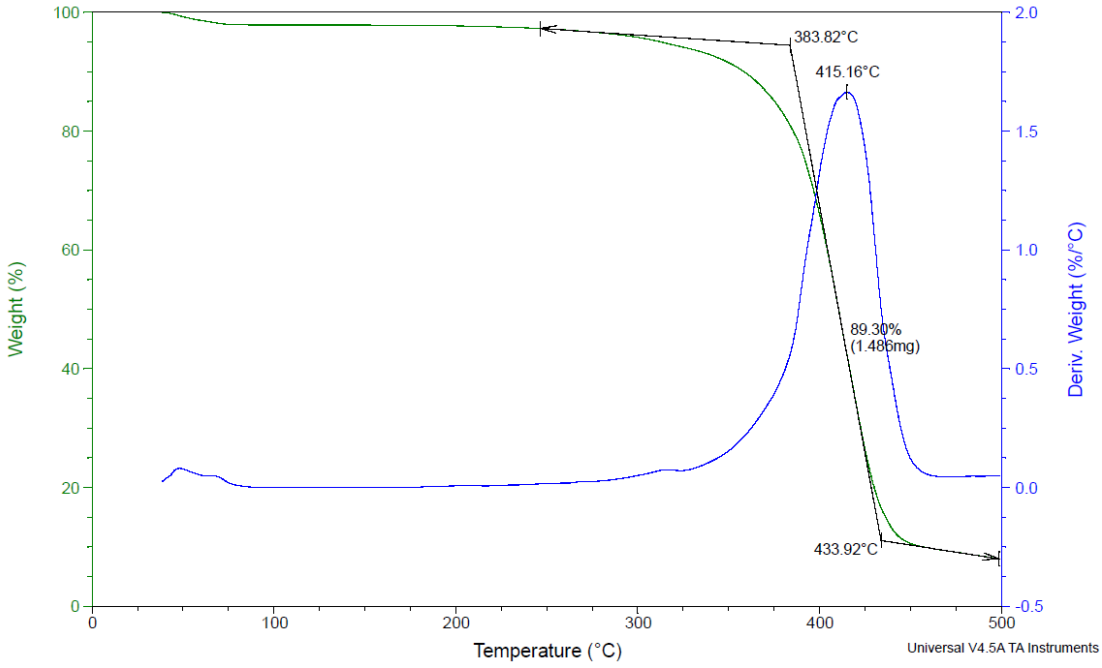

Figure S19. TGA profile of **poly-4**.

Figure S19. Recorded optical rotation of **poly-4.**

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[i] M. Winnacker, J. Sag, A. Tischner, B. Rieger, *Macromol. Rapid Commun.* 2017, **38**, 1600787.
[ii] S. M. Canham, L. E. Overman, P. S. Tanis, *Tetrahedron* 2011, **67**, 9837-9843.