

Step-growth polymerisation of alkyl acrylates via concomitant oxa-Michael and transesterification reactions

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Electronic Supporting Information

General Information

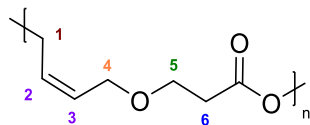
All experiments were performed under ambient conditions unless noted otherwise. Chemicals were purchased from Alfa Aesar, Carl Roth, Merck or TCI and were used as received. Hydroquinone stabilizers present in the alkyl acrylates were not removed. ^1H - and ^{13}C -NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer at 25 °C (^1H : 300.36 MHz; ^{13}C : 75.53 MHz). Chemical shifts δ are given in ppm relative to residual protons and carbon signals of the deuterated solvent.^[1] Deuterated solvents were obtained from Cambridge Isotope Laboratories Inc.

Size exclusion chromatography (SEC) was carried out on a system provided by Shimadzu (equipped with two separating columns from MZ-Gel SD plus, 500 Å and 100 Å, linear 5 μ ; UV detector (SPD-20A) and RI detector (RID-20A)) using THF as eluent. Poly(styrene) standards in the range of 350 to 17800 g/mol purchased from Polymer Standard Service were used for calibration.

Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) measurements were carried out on a Bruker UltrafleXtreme MALDI-TOF mass spectrometer (Bruker Daltonik, Germany). Samples were dissolved in THF (10 mg/mL), and mixed with a THF solution of 2,5-dihydroxyacetophenone (2,5-DHAP) as a matrix (30 mg/mL) and THF solution of NaTFA or KTFA as a cationizer (10 mg/mL), in a volume ratio of 1:10:3. A 0.4 μL of the prepared sample solution was spotted on a target plate (dried-droplet method). The reflective positive ion mode was used to acquire the samples' mass spectra. Calibration was performed externally with a mixture of PMMA standards (MALDI validation set PMMA, Fluka Analytical), covering the measured molecular weight range, and by using the nearest neighbour position method.

IR spectra were measured on a Bruker ALPHA FT-IR spectrometer. The spectra were recorded in the range from 4000-400 cm^{-1} with a resolution of 4 cm^{-1} and a sample scan time of 48 scans per spectrum. Processing and analysis were performed with Opus 7.5 software.

Preparation of Poly2/4 (according to Table 1, entry 4)



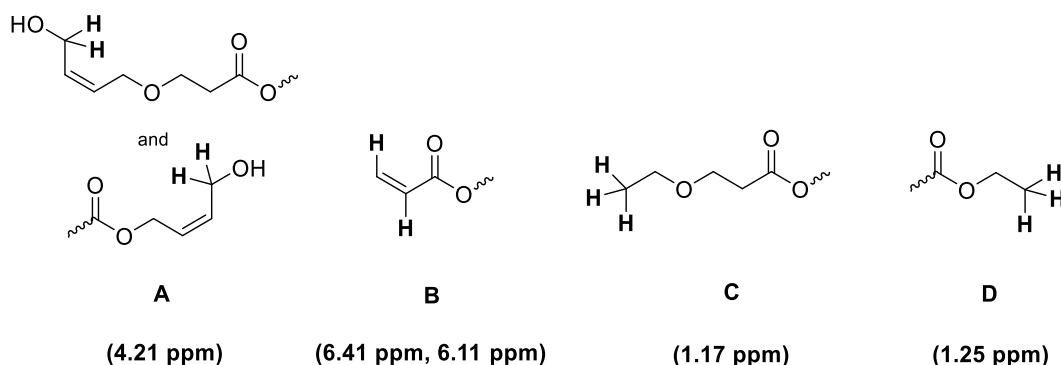
A sealed tube was charged with 186 mg (1.86 mmol, 1.00 equiv.) ethyl acrylate (**2**) and 167 mg (1.90 mmol, 1.02 equiv.) (*Z*)-2-butene-1,4-diol (**4**). The reaction mixture was heated to 50 °C and 5.9 mol% (16.6 mg, 0.105 mmol) DBU was added. After 2.5 h (full conversion of the α,β -unsaturated carbonyl compound monitored by $^1\text{H-NMR}$ spectroscopy) the reaction temperature was elevated to 80 °C and the reaction tube was opened. After a total reaction time of 24 h the reaction mixture was dissolved in 5 mL CH_2Cl_2 and was extracted with 1 M HCl (1 x 5 mL). The organic layer was washed with brine (2 x 5 mL), dried over Na_2SO_4 and filtered. The solvent was removed by vacuum yielding a light yellow viscous liquid.

$^1\text{H-NMR}$ (300.36 MHz, CDCl_3): δ = 6.41 (d, CH, $^3J_{\text{HH(E)}} = 17.4$ Hz, 8% end group), 6.11 (dd, CH, $^3J_{\text{HH}} = 17.1, 9.8$ Hz, 8% end group), **5.70** (d, CH (2,3), **2.12H**), **4.68** (dd, CH₂ (1), $^3J_{\text{HH}} = 12.9, 5.0$ Hz, **1.88H**), 4.21 (dd, CH₂, $^3J_{\text{HH}} = 16.8, 6.2$ Hz, 72% end group), **4.14 – 3.95** (m, CH₂ (4), **1.91H**), **3.69** (t, CH₂ (5), **1.93H**), 3.48 (q, -COO-CH₂-CH₂-O-CH₂-CH₃, 8% end group), **2.58** (t, CH₂ (6), **2H**), 1.25 (t, -COO-CH₂-CH₃, $^3J_{\text{HH}} = 7.2$ Hz, 12% end group), 1.17 (t, -COO-CH₂-CH₂-O-CH₂-CH₃, 8% end group) ppm.

$^{13}\text{C-NMR}$ (75.53 MHz, CDCl_3): δ = **171.63, 171.34** (COO), 133.73, 132.70 (-CH₂-CH=CH-CH₂-OH end group), **130.77, 130.63, 129.47, 129.38, 128.09, 127.99, 126.81, 126.67** (CH (2,3)), 125.42, **66.75, 66.65** (CH₂ (4)), **65.75, 65.63** (CH₂ (5)), **60.43, 60.23** (CH₂ (1)), 58.75, 58.47 (-CH₂-CH=CH-CH₂-OH end group), **35.09, 35.09** (CH₂ (6)), 15.15 (-COO-CH₂-CH₃ end group), 14.28 (-COO-CH₂-CH₂-O-CH₂-CH₃ end group) ppm.

Peaks assigned to the repeating units are printed in bold.

Determination of end group distribution and calculation of average number molecular mass:



ESI Scheme 1: End groups of **poly2/4** detected by $^1\text{H-NMR}$ spectroscopy.

Protons at 2.58 ppm ($\text{CH}_2(6)$) were referenced to 2.

ESI Table 1: Calculation of end group distribution via $^1\text{H-NMR}$ integration.

	A	B	C	D	Total number of end groups ^a
Integral $^1\text{H-NMR}$ ^b	0.51 ^c	0.06	0.053	0.087	0.71
End group distribution [%] ^d	72	8	8	12	100

^a Total number of end groups = sum of integrals referring to end groups A-D; ^b the integrals of the end group A-D were recalculated if necessary in order to refer to 2 protons (e.g. C: $0.08/3 \times 2 = 0.053$); ^c as the signal of end group D overlaps with end group A, the integral of D was subtracted from the integral of A; ^d (calculated integral of end group)/total number of end groups*100.

Integration of $^1\text{H-NMR}$ spectra was used to estimate average number molecular masses of the oligomers. Transesterification reactions are not considered in the calculations.

Protons at 2.58 ppm ($\text{CH}_2(6)$) were referenced to 2. However, the CH_2 group of the *oxa*-Michael addition of end group C is overlapping with CH_2 signals of the repeating unit (RU). This was considered in the calculation by subtracting the value referring to the CH_2 group of end group C from the 2 protons ($2 - \text{integral}(\text{C})$)*.

$$\text{MW (RU)} = 142.15 \text{ Da}$$

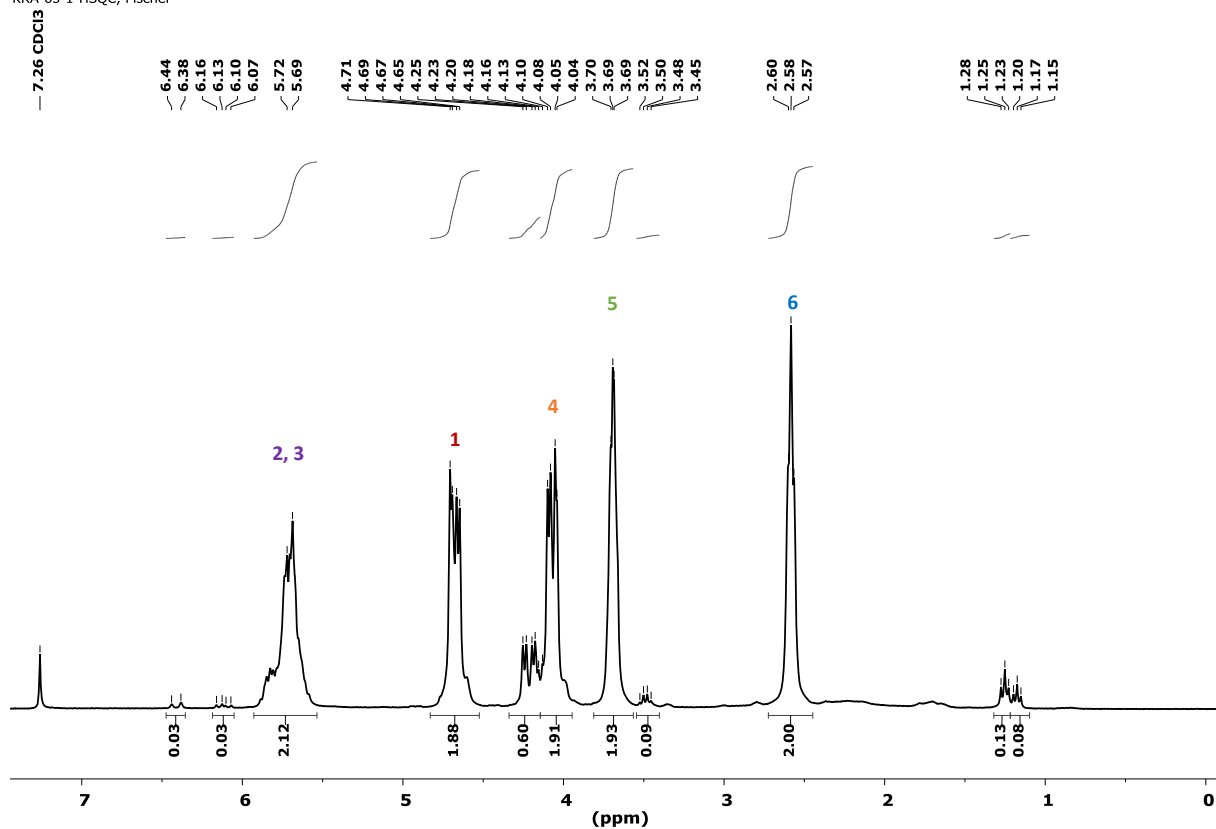
ESI Table 2: Determination of average number molecular mass of **poly2/4**.

One end group per oligomer	Calculated value of CH_2 signal of the RU*	n ^a	Molecular mass [Da] (without end groups) ^b
0.355	1.947	5.5	779

^a Degree of polymerization (n) = (calculated value of CH_2 signal of the RU)/(one end group of the oligomer); ^b $n \times \text{MW (RU)}$.

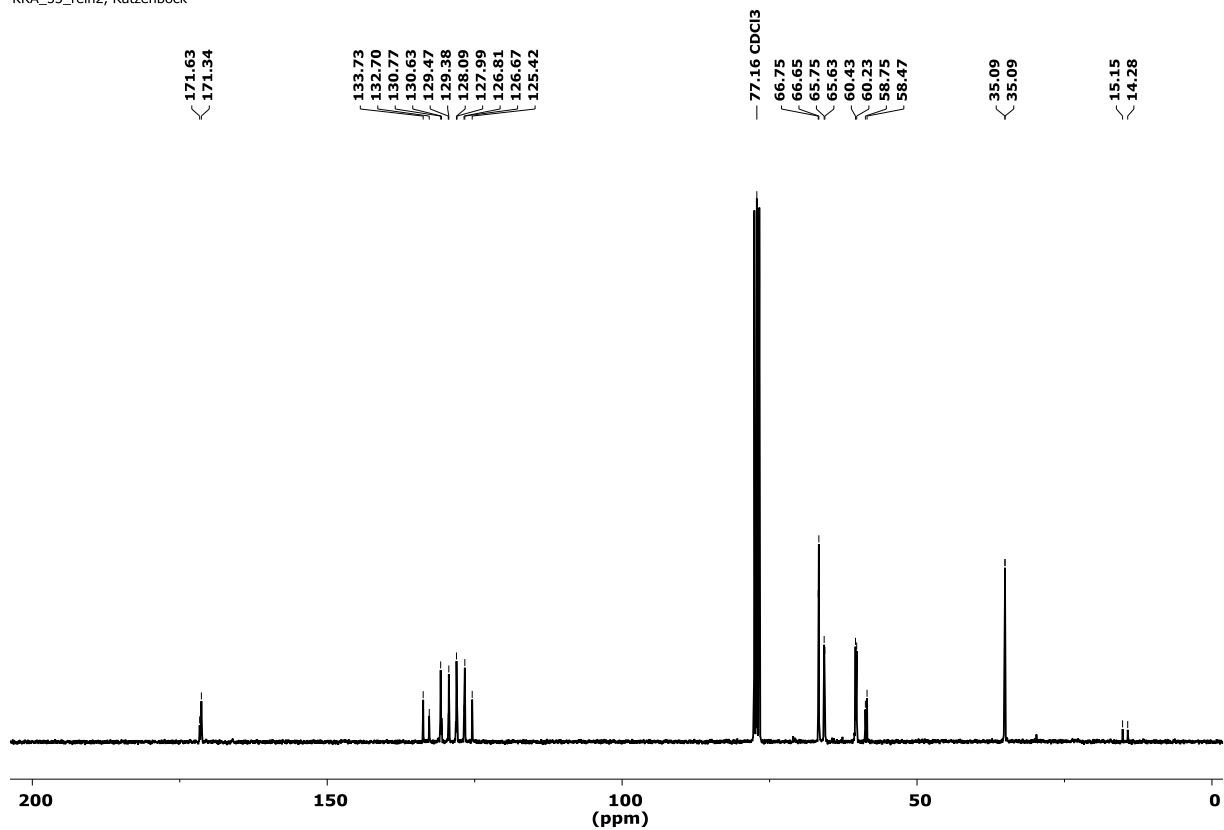
The same method of calculation was applied for all further experiments.

KRA-65-1-HSQC, Fischer

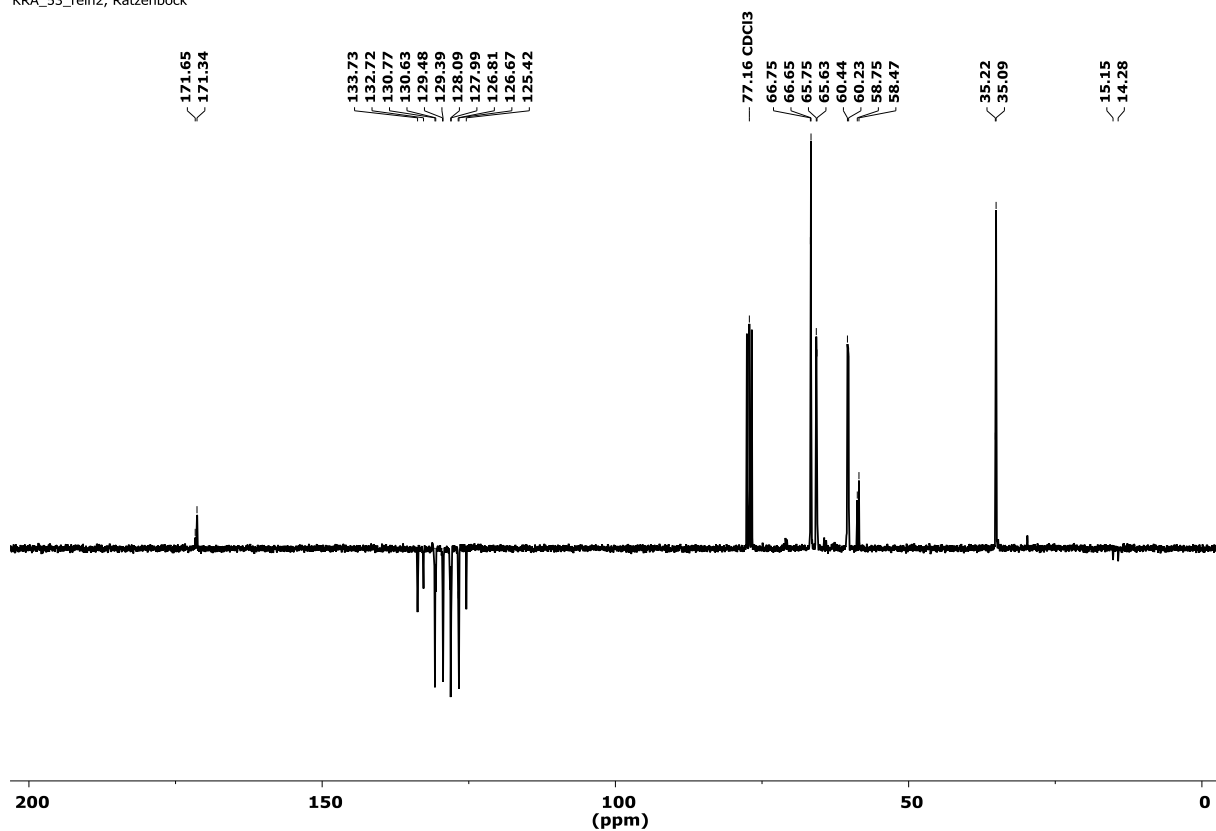


ESI Figure 1: ¹H-NMR spectrum of **poly2/4** after work-up.

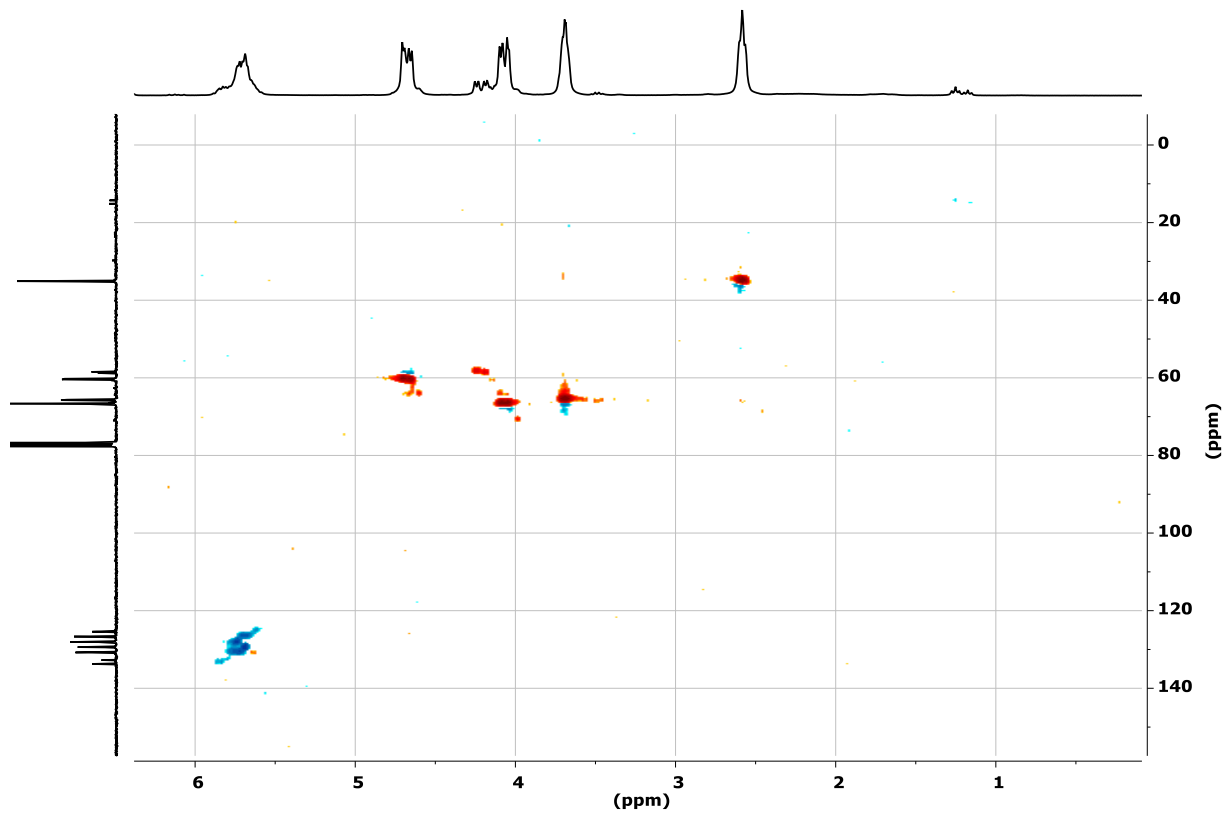
KRA_53_rein2, Ratzenbock



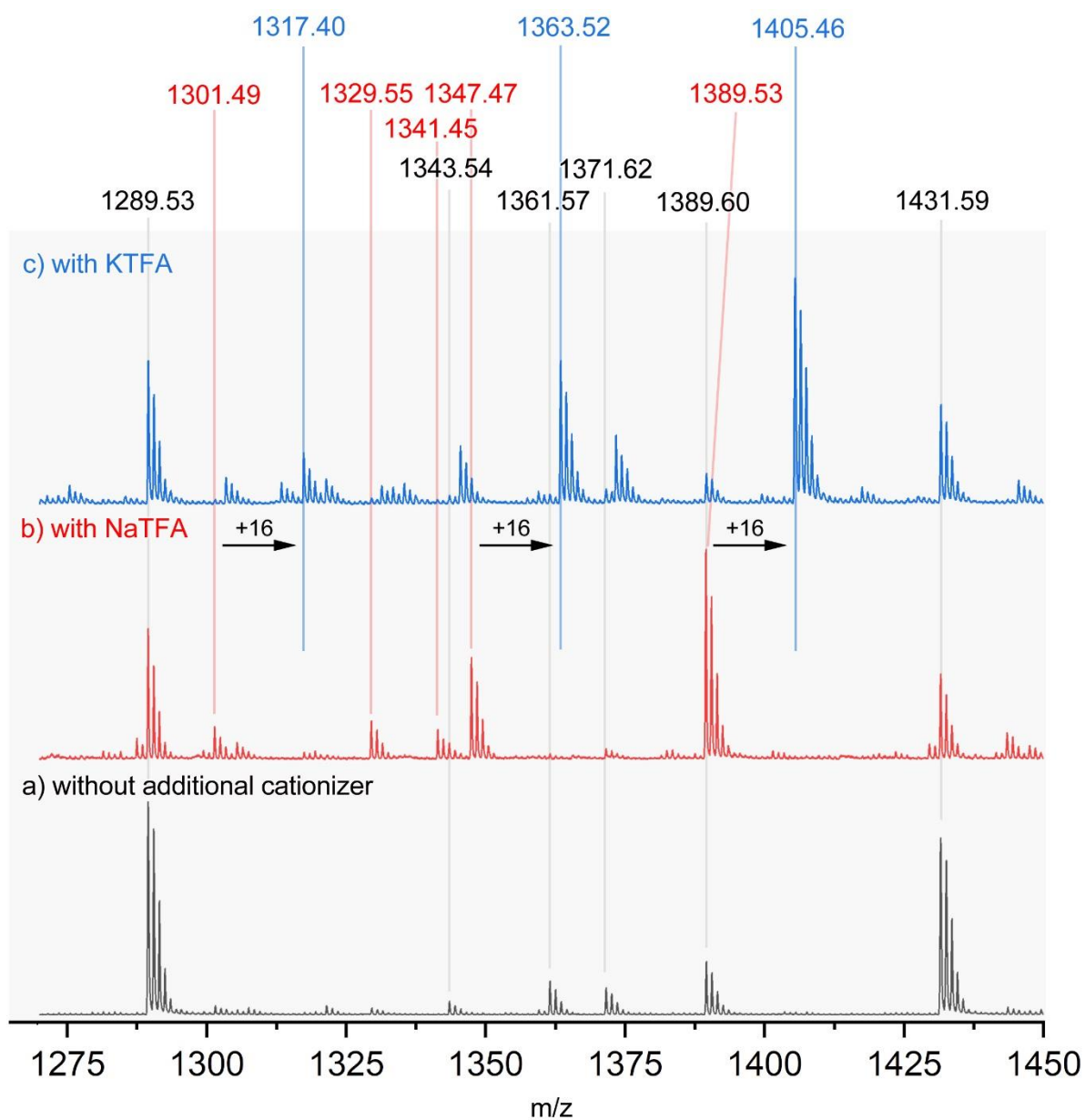
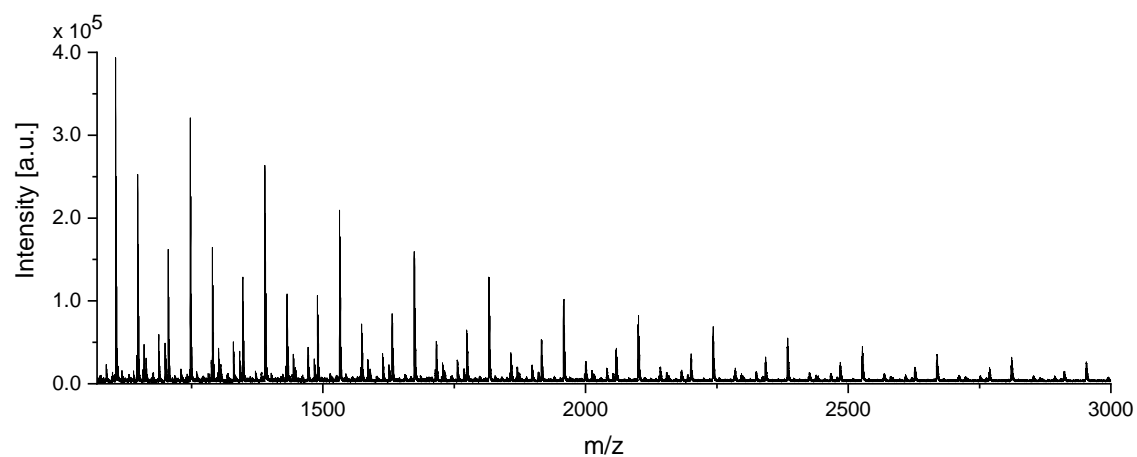
ESI Figure 2: ¹³C-NMR spectrum of **poly2/4** after work-up.



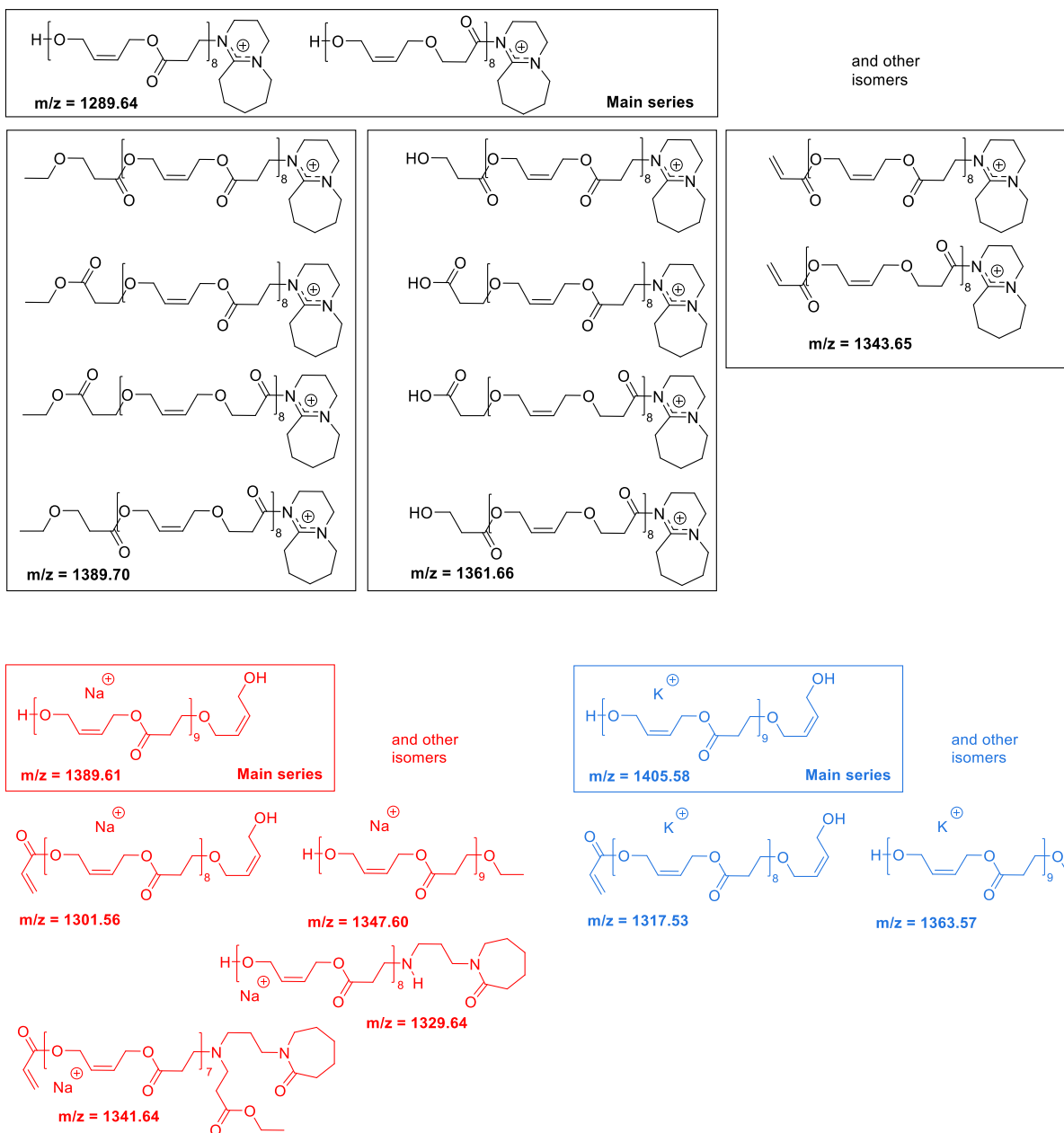
ESI Figure 3: ¹³C/APT-NMR spectrum of **poly2/4** after work-up.



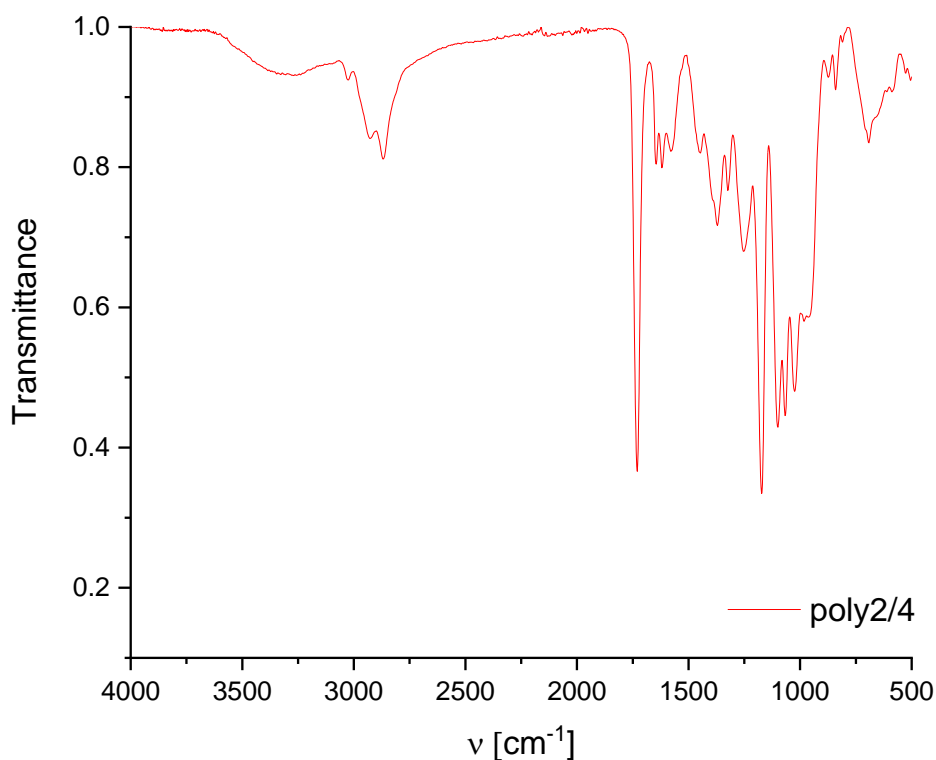
ESI Figure 4: HSQC spectrum of **poly2/4** in CDCl₃ after work-up.



ESI Figure 5: top: MALDI-TOF mass spectra of **poly2/4** with NaTFA as cationizer; bottom: MALDI-TOF mass spectra of **poly2/4** in detail recorded under different conditions (a-c).



ESI Figure 6: Various structures of **poly2/4** observed in MALDI-TOF MS.



ESI Figure 7: IR spectrum of **poly2/4**. IR bands at 1648 cm^{-1} and 1575 cm^{-1} are significant for DBU and its decomposition product in presence of water.

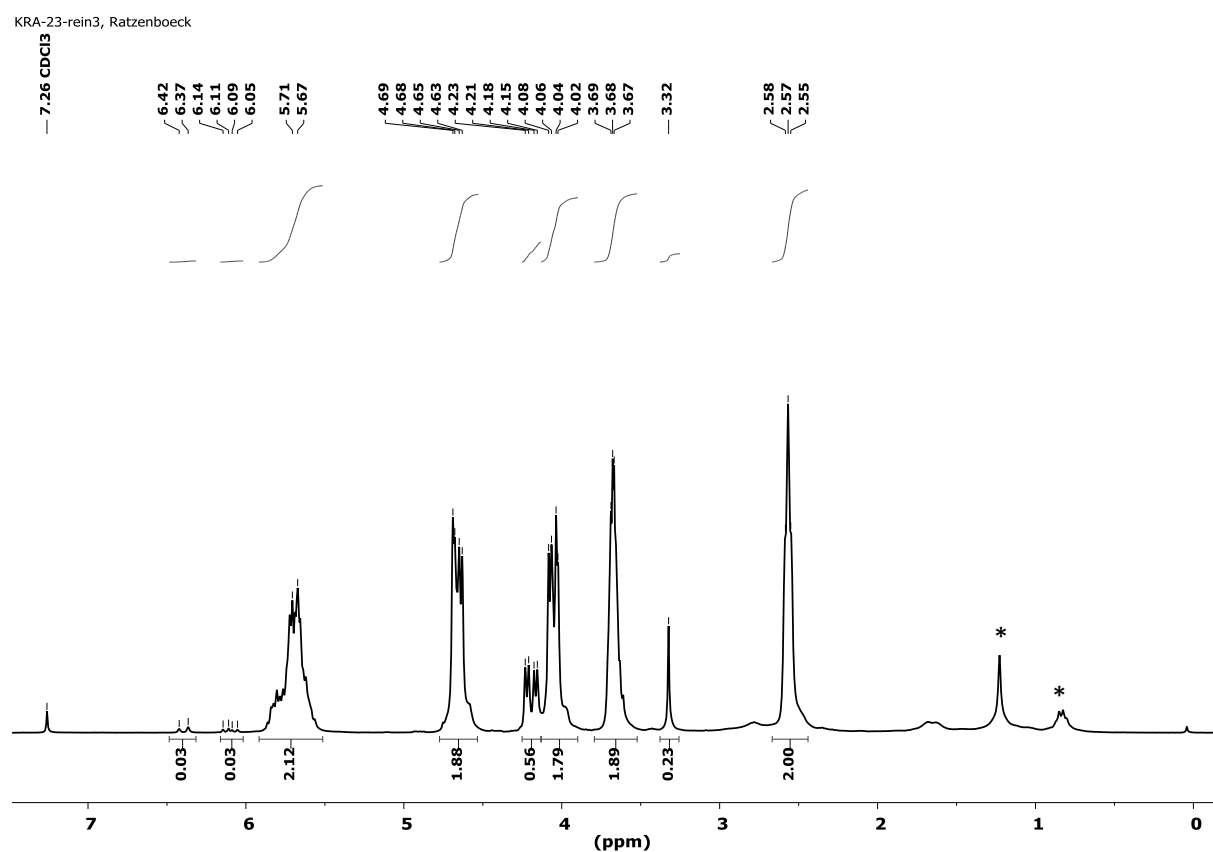
Preparation of Poly1/4 (according to Table 1, entry 2)

A sealed tube was charged with 108 mg (1.26 mmol, 1.00 equiv.) methyl acrylate (**1**) and 119 mg (1.35 mmol, 1.07 equiv.) (*Z*)-2-butene-1,4-diol (**4**). The reaction mixture was heated to $50\text{ }^{\circ}\text{C}$ and 5.3 mol% (10.2 mg, 0.1067 mmol) DBU was added. After 1.2 h (full conversion of the α,β -unsaturated carbonyl compound monitored by $^1\text{H-NMR}$ spectroscopy) the reaction temperature was elevated to $80\text{ }^{\circ}\text{C}$ and the reaction tube was opened. After a total reaction time of 24 h the reaction mixture was dissolved in 5 mL CH_2Cl_2 and was extracted with 1 M HCl (1 x 5 mL). The organic layer was washed with brine (2 x 5 mL), dried over Na_2SO_4 and filtered. The solvent was removed by vacuum yielding a light yellow viscous liquid.

$^1\text{H-NMR}$ (300.36 MHz, CDCl_3): $\delta = 6.39$ (d, CH, $^3J_{\text{HH(E)}} = 17.1$ Hz, 8% end group), 6.10 (dd, CH, $^3J_{\text{HH}} = 17.2, 10.3$ Hz, 8% end group), **5.69 (m, CH (2,3), 2.12H)**, **4.66 (dd, CH₂ (1), $^3J_{\text{HH}} = 13.0, 4.7$ Hz, 1.88H)**, 4.19 (dd, CH₂, $^3J_{\text{HH}} = 16.6, 6.3$ Hz, 72% end group), **4.05 (dd, CH₂ (4), $^3J_{\text{HH}} = 13.2, 4.6$ Hz, 1.79H)**, **3.68 (t, CH₂ (5), 1.89H)**, 3.32 (s, $-\text{COO}-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_3$, 20% end group), **2.57 (t, CH₂ (6), $^3J_{\text{HH}} = 5.1$ Hz, 2H)** ppm.

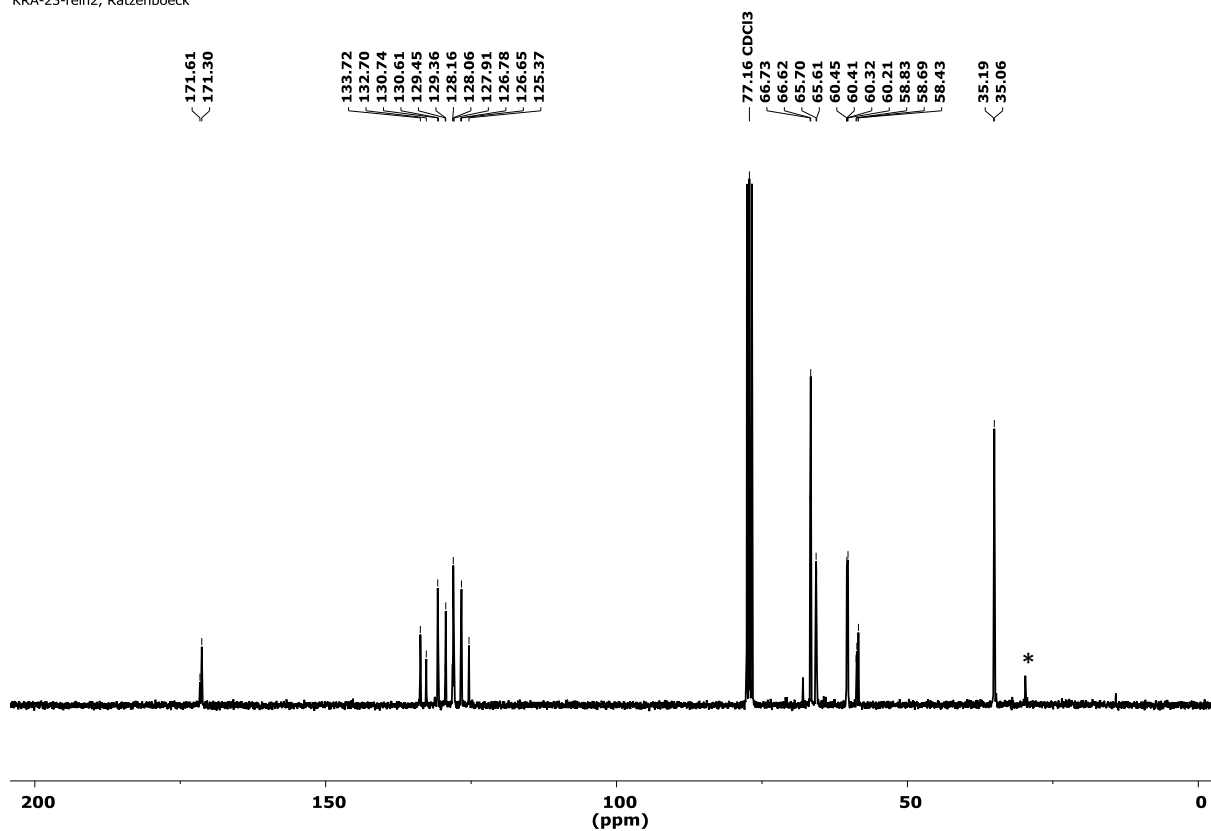
^{13}C -NMR (75.53 MHz, CDCl_3): $\delta = 171.61, 171.30$ (COO), $133.72, 132.70$ ($-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{OH}$ end group), **$133.72, 132.70, 130.74, 130.61, 129.36, 128.16, 128.06, 127.91, 126.78, 126.65, 125.37$** (CH (2,3)), **$66.73, 66.62$** (CH_2 (4)), **$65.70, 65.61$** (CH_2 (5)), **$60.45, 60.41, 60.32, 60.21$** (CH_2 (1)), 58.83 ($-\text{COO}-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_3$ end group), $58.69, 58.43$ ($-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{OH}$ end group), **$35.19, 35.06$** (CH_2 (6)) ppm.

Peaks assigned to the repeating units are printed in bold.



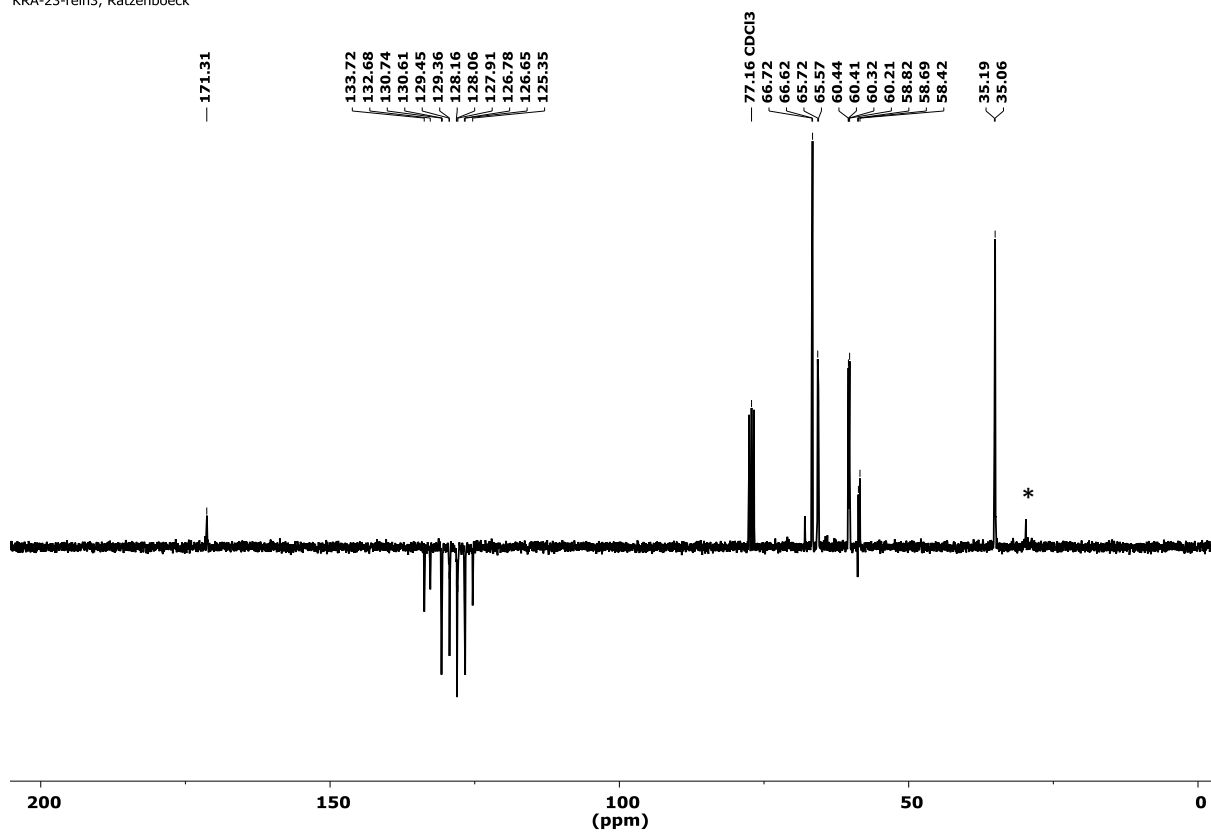
ESI Figure 8: ^1H -NMR spectrum of **poly1/4** after work-up; * denotes H grease.^[1]

KRA-23-rein2, Ratzenboeck

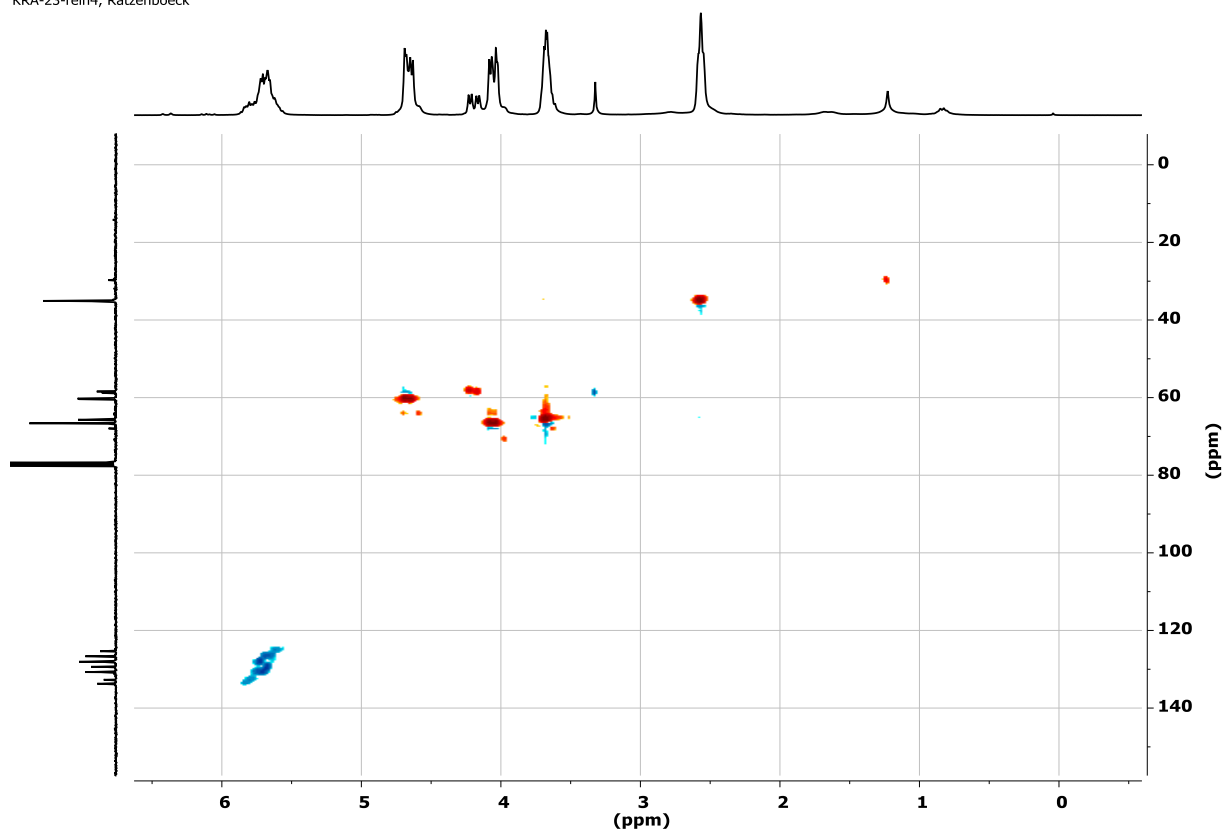


ESI Figure 9: ^{13}C -NMR spectrum of **poly1/4** after work-up; * denotes H grease.^[1]

KRA-23-rein3, Ratzenboeck

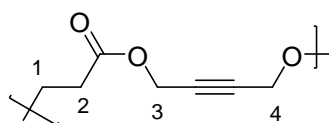


ESI Figure 10: ^{13}C /APT-NMR spectrum of **poly1/4** after work-up; * denotes H grease.^[1]

ESI Figure 11: HSQC spectrum of **poly1/4** in CDCl_3 after work-up.

Preparation of **poly2/5** (according to Table 2, entry 3)

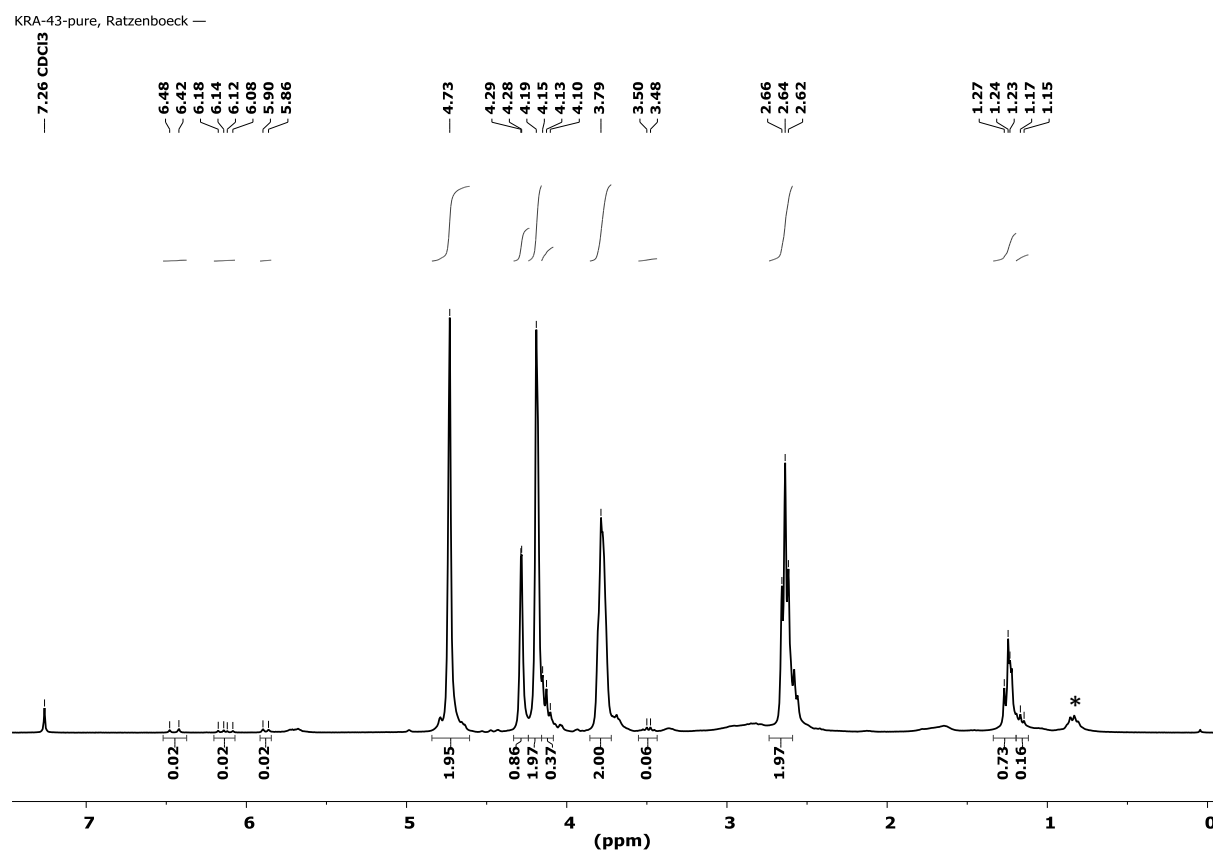
A sealed tube was charged with 128 mg (1.28 mmol, 1.00 equiv.) ethyl acrylate (**2**) and 114 mg (1.32 mmol, 1.03 equiv.) 1,4-butyndiol (**5**). The reaction mixture was heated to 50 °C and 5.2 mol% (10.2 mg, 0.067 mmol) DBU was added whereupon the mixture turned orange. After 0.5 h (full conversion of the α,β -unsaturated carbonyl compound monitored by $^1\text{H-NMR}$ spectroscopy) the reaction temperature was elevated to 80 °C and the reaction tube was opened. After a total reaction time of 24 h the reaction mixture was dissolved in 5 mL CH_2Cl_2 and was extracted with 1 M HCl (1 x 5 mL). The organic layer was washed with brine (2 x 5 mL), dried over Na_2SO_4 and filtered. The solvent was removed by vacuum yielding an orange viscous liquid.



$^1\text{H-NMR}$ (300.36 MHz, CDCl_3): $\delta = 6.45$ (d, CH, $^3J_{\text{HH(E)}} = 17.3$ Hz, 3% end group), 6.13 (dd, CH, $^3J_{\text{HH}} = 17.0, 10.3$ Hz, 3% end group), 5.88 (d, CH, $^3J_{\text{HH(Z)}} = 10.4$ Hz, 3% end group), **4.73** (s, **CH₂** (3), **1.95H**), 4.29 (d, -O-CH₂-C \equiv C-CH₂-OH, 62% end group), **4.19** (s, **CH₂** (4), **1.97H**), 4.14 (q, -COO-CH₂-CH₃, 27% end group), **3.86 – 3.72** (m, **CH₂** (1), **2H**), 3.49 (q, -OOC-CH₂-CH₂-O-CH₂-CH₃, 0.07H, 8% end group), **2.64** (t, **CH₂** (2), $^3J_{\text{HH}} = 6.1$ Hz, **1.97H**), 1.25 (t, -COO-CH₂-CH₃, 27% end group), 1.17 (t, -OOC-CH₂-CH₂-O-CH₂-CH₃, 8% end group) ppm.

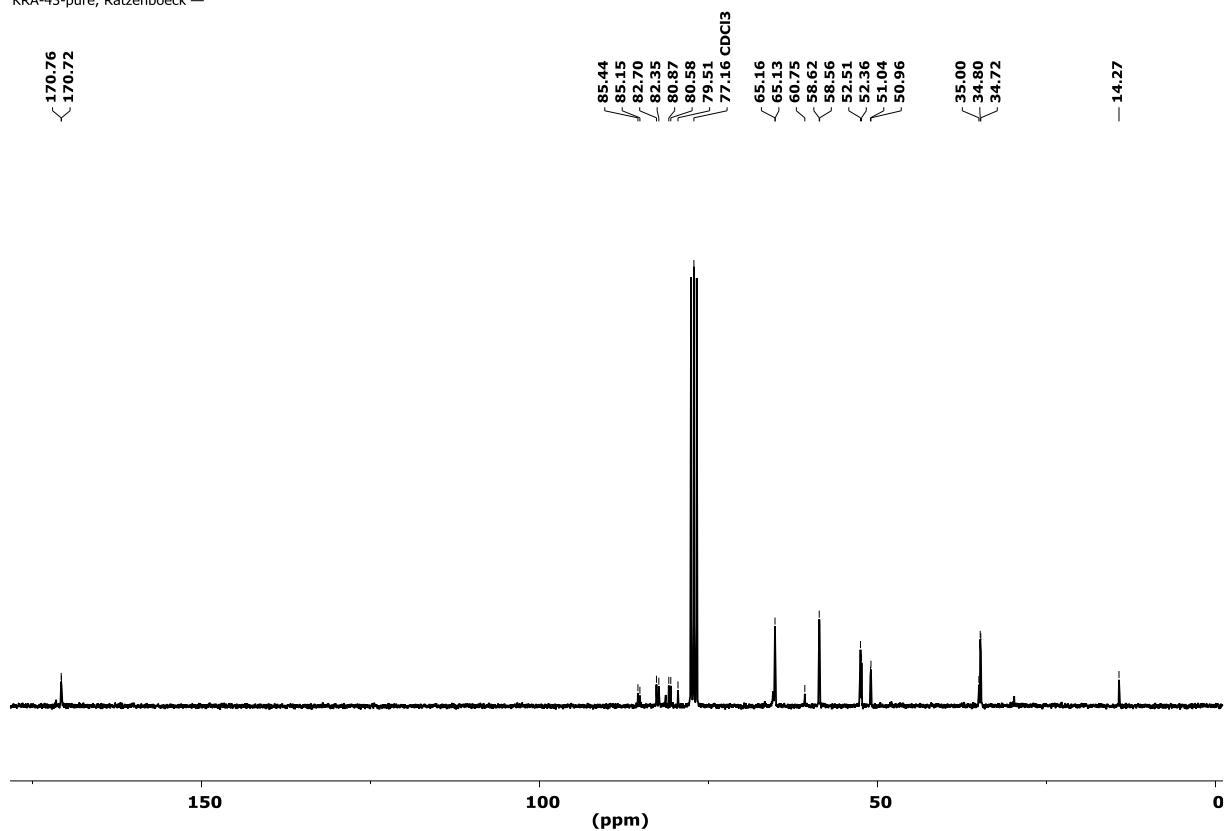
$^{13}\text{C-NMR}$ (75.53 MHz, CDCl_3): $\delta = 170.76, 170.72$ (COO), 85.44, 85.15 (-O-CH₂-C \equiv C-CH₂-OH end group), **82.70, 82.35, 80.87, 80.58**(-CH₂-C \equiv C-CH₂-), 79.51, **65.16, 65.13** (CH₂ (1)), 60.75, 58.62, 58.56 (CH₂ (4)), **52.51, 52.36** (CH₂ (3)), 51.04, 50.96 (-O-CH₂-C \equiv C-CH₂-OH end group), 35.00, **34.80, 34.72** (CH₂ (2)), 14.27 (-COO-CH₂-CH₃ end group) ppm.

Peaks assigned to the repeating units are printed in bold.



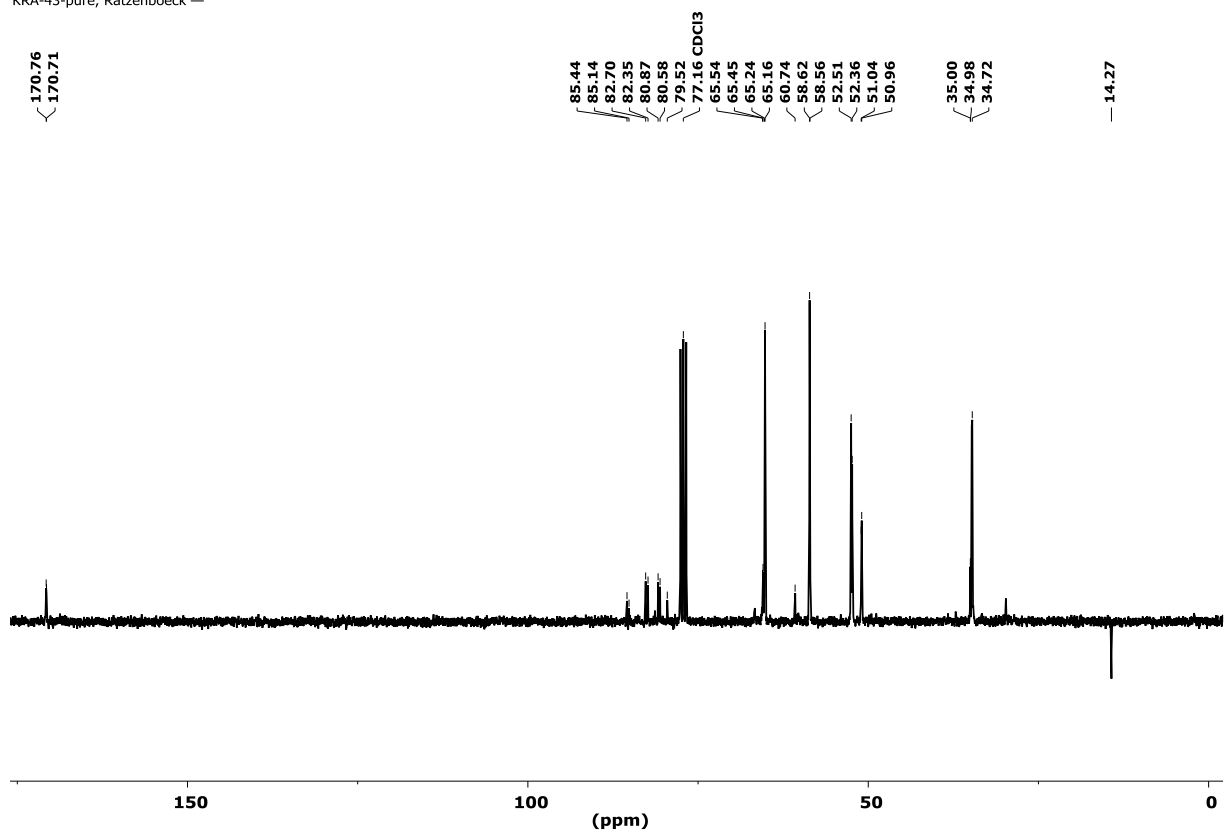
ESI Figure 12: $^1\text{H-NMR}$ spectrum of **poly2/5** after work-up; * denotes H grease.^[1]

KRA-43-pure, Ratzenboeck —

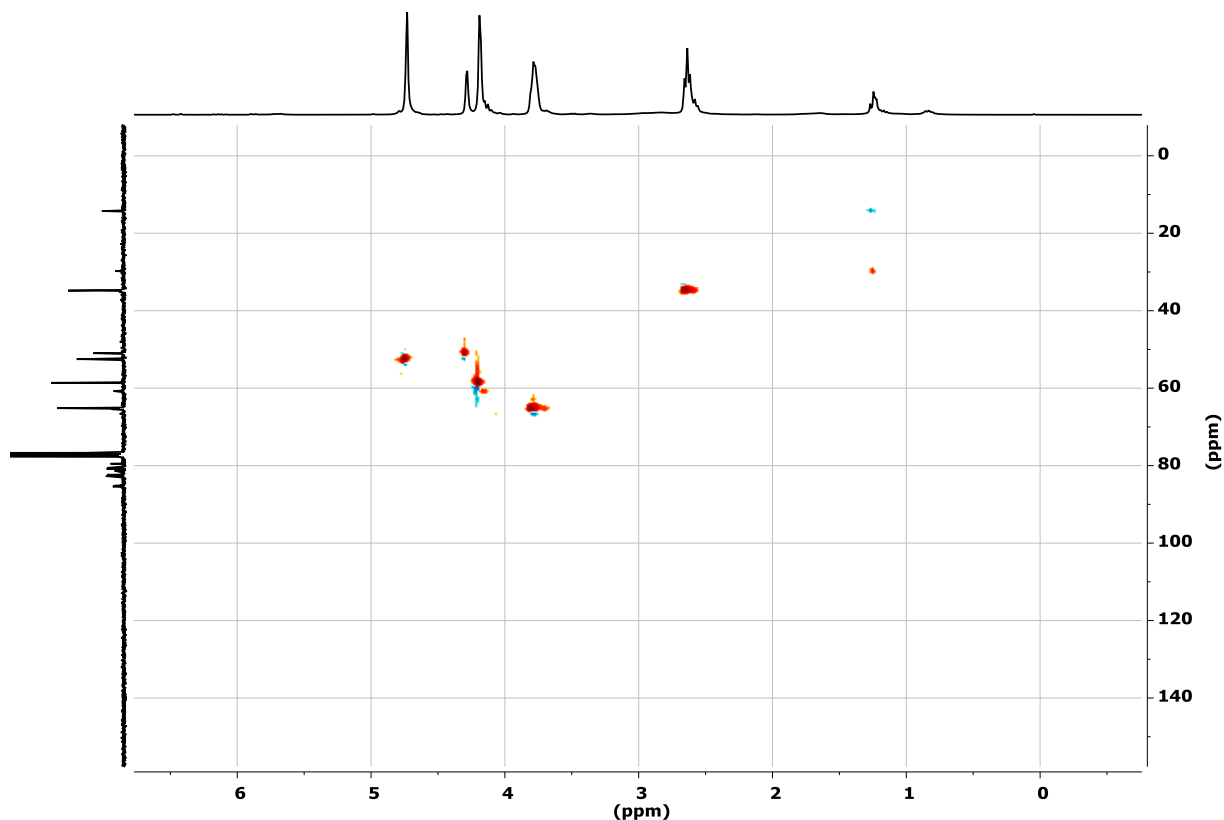


ESI Figure 13: ^{13}C -NMR spectrum of **poly2/5** after work-up.

KRA-43-pure, Ratzenboeck —



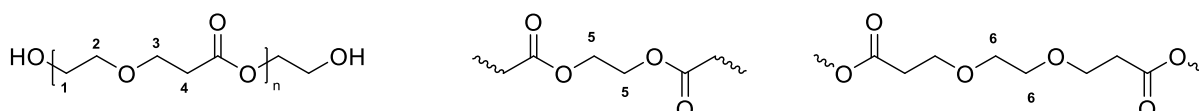
ESI Figure 14: ^{13}C /APT-NMR spectrum of **poly2/5** after work-up.

ESI Figure 15: HSQC spectrum of **poly2/5** in CDCl_3 after work-up.

Preparation of **poly2/6** (according to Table 2, entry 4)

A sealed tube was charged with 161 mg (1.61 mmol, 1.00 equiv.) ethyl acrylate (**2**) and 101 mg (1.63 mmol, 1.01 equiv.) ethylene glycol (**6**). The reaction mixture was heated to 50 °C and 5.3 mol% (13.0 mg, 0.085 mmol) DBU was added. After 2.5 h (full conversion of the α,β -unsaturated carbonyl compound monitored by $^1\text{H-NMR}$ spectroscopy) the reaction temperature was elevated to 80 °C and the reaction tube was opened. After a total reaction time of 24 h the reaction mixture was dissolved in 5 mL CH_2Cl_2 and was extracted with 1 M HCl (1 x 5 mL). The organic layer was washed with brine (2 x 5 mL), dried over Na_2SO_4 and filtered. The solvent was removed by vacuum yielding a colorless viscous liquid.

further fragments:



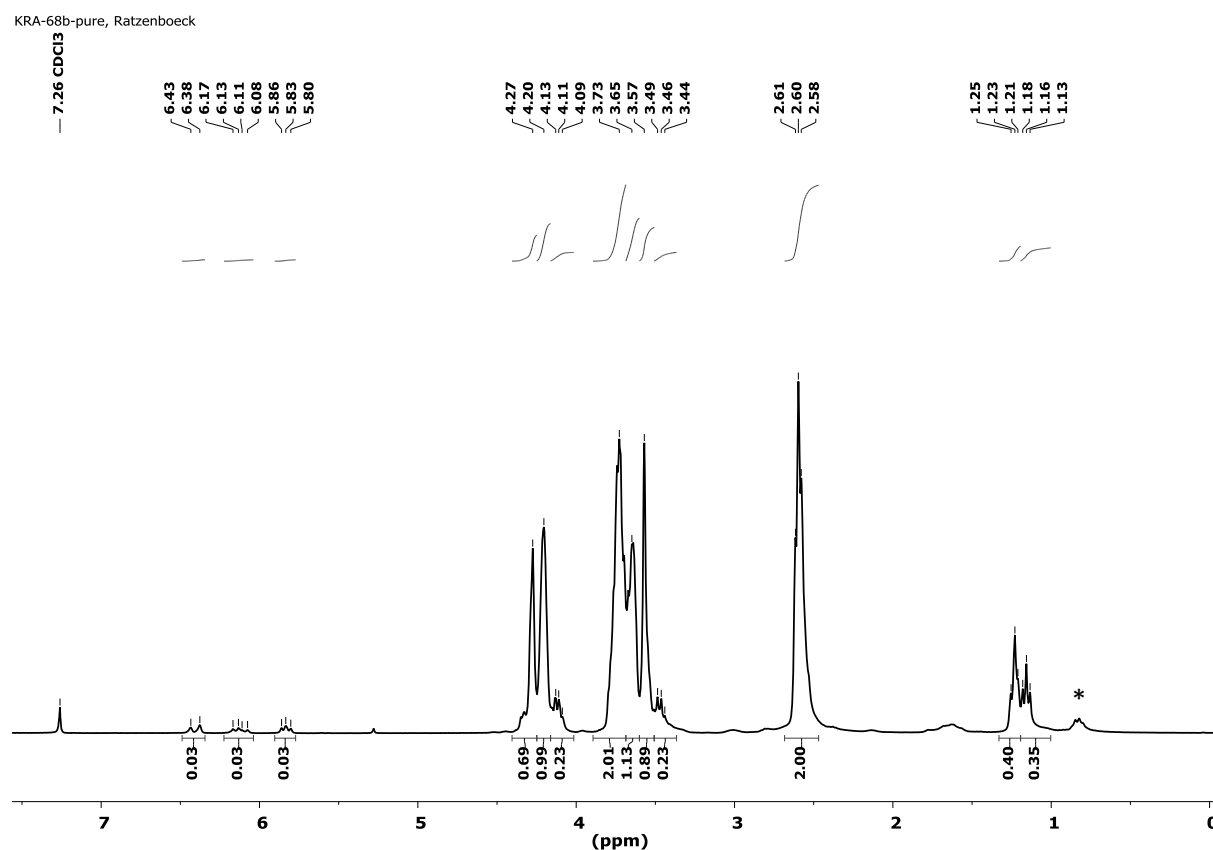
$^1\text{H-NMR}$ (300.36 MHz, CDCl_3): δ = 6.41 (d, CH, $^3J_{\text{HH(E)}} = 17.1$ Hz), 6.12 (dd, CH, $^3J_{\text{HH}} = 17.2$, 10.4 Hz), 5.83 (t, CH, $^3J_{\text{HH(Z)}} = 8.8$ Hz), 4.27 (s, CH_2 (5) and $-\text{O-CH}_2\text{-CH}_2\text{-OH}$ end group, 0.69H),

4.20 (s, CH_2 (1), **0.99H**), 4.15 – 4.05 (q, $-\text{COO}-\text{CH}_2-\text{CH}_3$ end group), **3.73** (m, CH_2 (3), **2.01H**), **3.65** (m, CH_2 (2), **1.13H**), 3.57 (s, CH_2 (6) and $-\text{O}-\text{CH}_2-\text{CH}_2-\text{OH}$ end group, 0.89H), 3.47 (q, $-\text{OOC}-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_3$ end group), **2.60** (t, CH_2 (4), $J = 5.5$ Hz, **2H**), 1.23 (t, $J = 6.5$ Hz, $-\text{COO}-\text{CH}_2-\text{CH}_3$ end group), 1.16 (t, $-\text{OOC}-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_3$ end group) ppm.

^{13}C -NMR (75.53 MHz, CDCl_3): $\delta = 171.88, 171.43, 171.25$ (COO), 72.16, 70.36 (CH_2 (6)), **68.91** (CH_2 (2)), **66.77, 66.67, 66.53**, 66.24 ($-\text{OOC}-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_3$ end group), **65.79, 65.70** (CH_2 (3)), **63.59** (CH_2 (1)), 62.41, 62.31 (CH_2 (5)), 61.63, 60.95, 60.62 ($-\text{COO}-\text{CH}_2-\text{CH}_3$ end group), **35.25, 35.13, 35.01, 34.97, 34.89** (CH_2 (4)), 15.15 ($-\text{OOC}-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_3$ end group), 14.27 ($-\text{COO}-\text{CH}_2-\text{CH}_3$ end group) ppm.

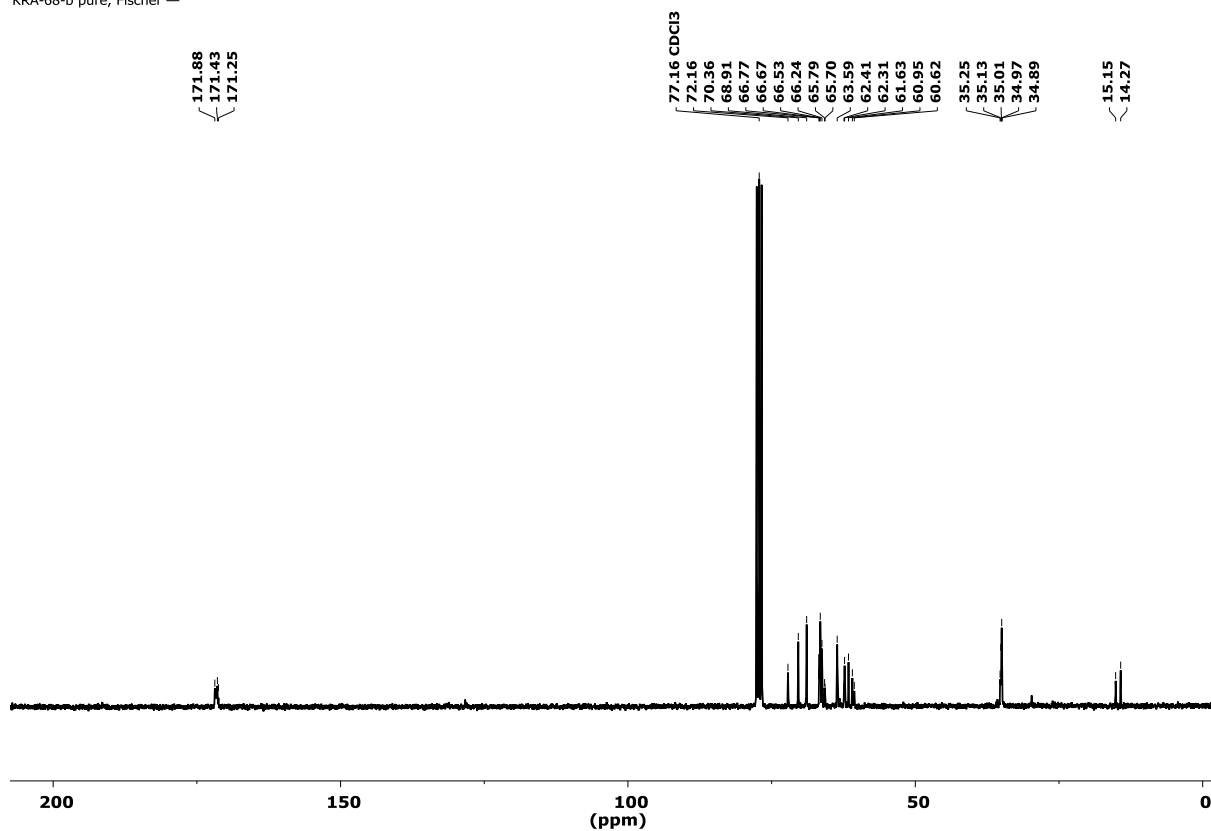
Peaks assigned to the repeating units are printed in bold.

End group distribution for **poly2/6** could not be determined by NMR spectroscopy as overlapping signals interfere with integration.



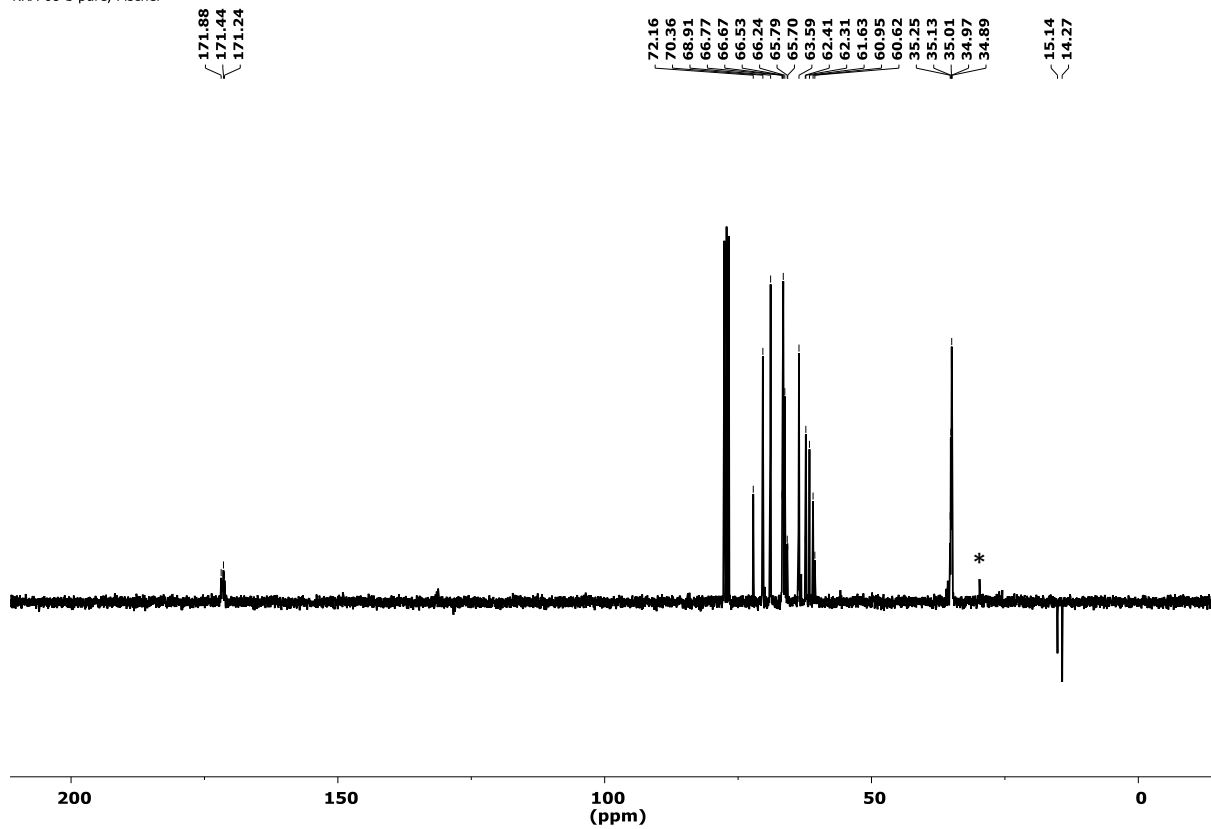
ESI Figure 16: ^1H -NMR spectrum of **poly2/6** after work-up; * denotes H grease.^[1]

KRA-68-b pure, Fischer —

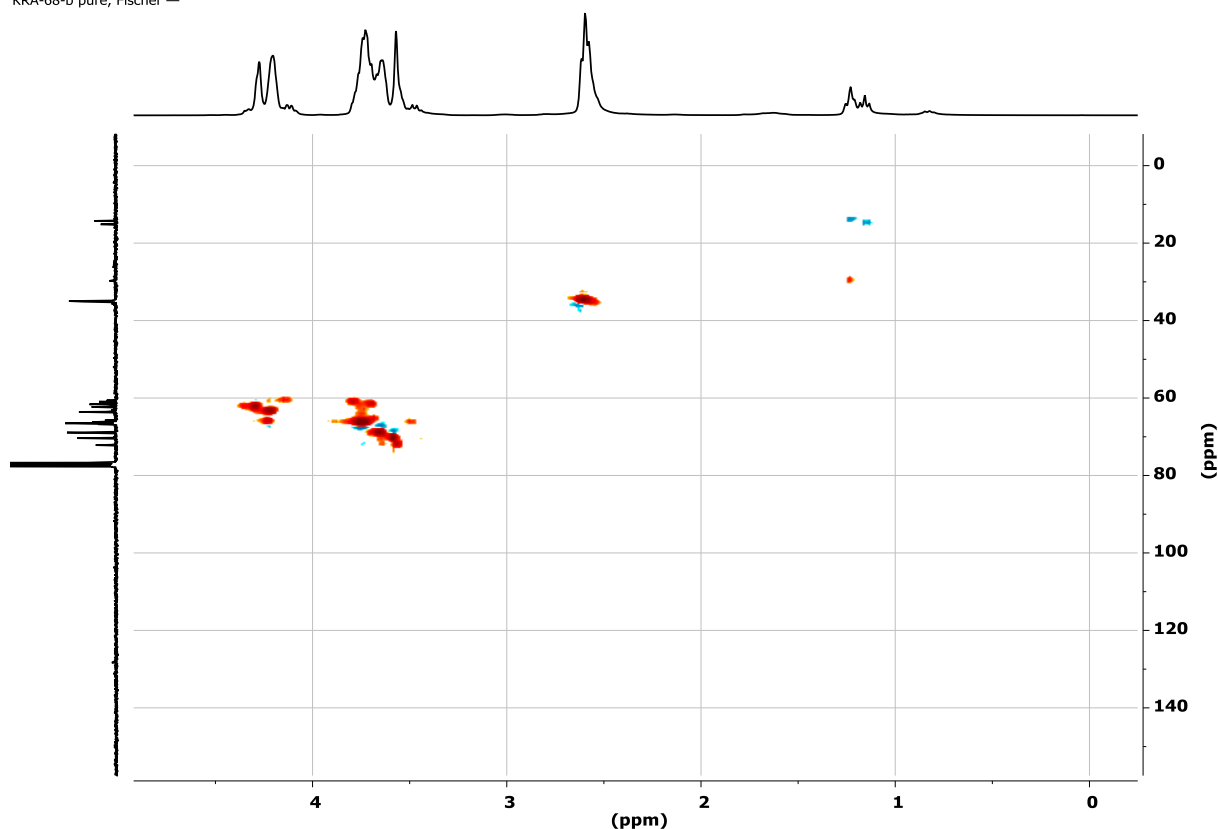


ESI Figure 17: ^{13}C -NMR spectrum of **poly2/6** after work-up.

KRA-68-b pure, Fischer —

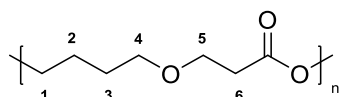


ESI Figure 18: ^{13}C /APT-NMR spectrum of **poly2/6** after work-up, * denotes H grease.^[1]

ESI Figure 19: HSQC spectrum of **poly2/6** in CDCl_3 after work-up.

Preparation of **poly2/7** (according to Table 2, entry 5)

A sealed tube was charged with 160 mg (1.59 mmol, 1.00 equiv.) ethyl acrylate (**2**) and 155 mg (1.72 mmol, 1.08 equiv.) 1,4-butane diol (**7**). The reaction mixture was heated to 50 °C and 5.8 mol% (14.0 mg, 0.092 mmol) DBU was added. After 5 h (full conversion of the α,β -unsaturated carbonyl compound monitored by $^1\text{H-NMR}$ spectroscopy) the reaction temperature was elevated to 80 °C and the reaction tube was opened after 23 h. After a total reaction time of 24 h the reaction mixture was dissolved in 5 mL CH_2Cl_2 and was extracted with 1 M HCl (1 x 5 mL). The organic layer was washed with brine (2 x 5 mL), dried over Na_2SO_4 and filtered. The solvent was removed by vacuum yielding a colorless viscous liquid.

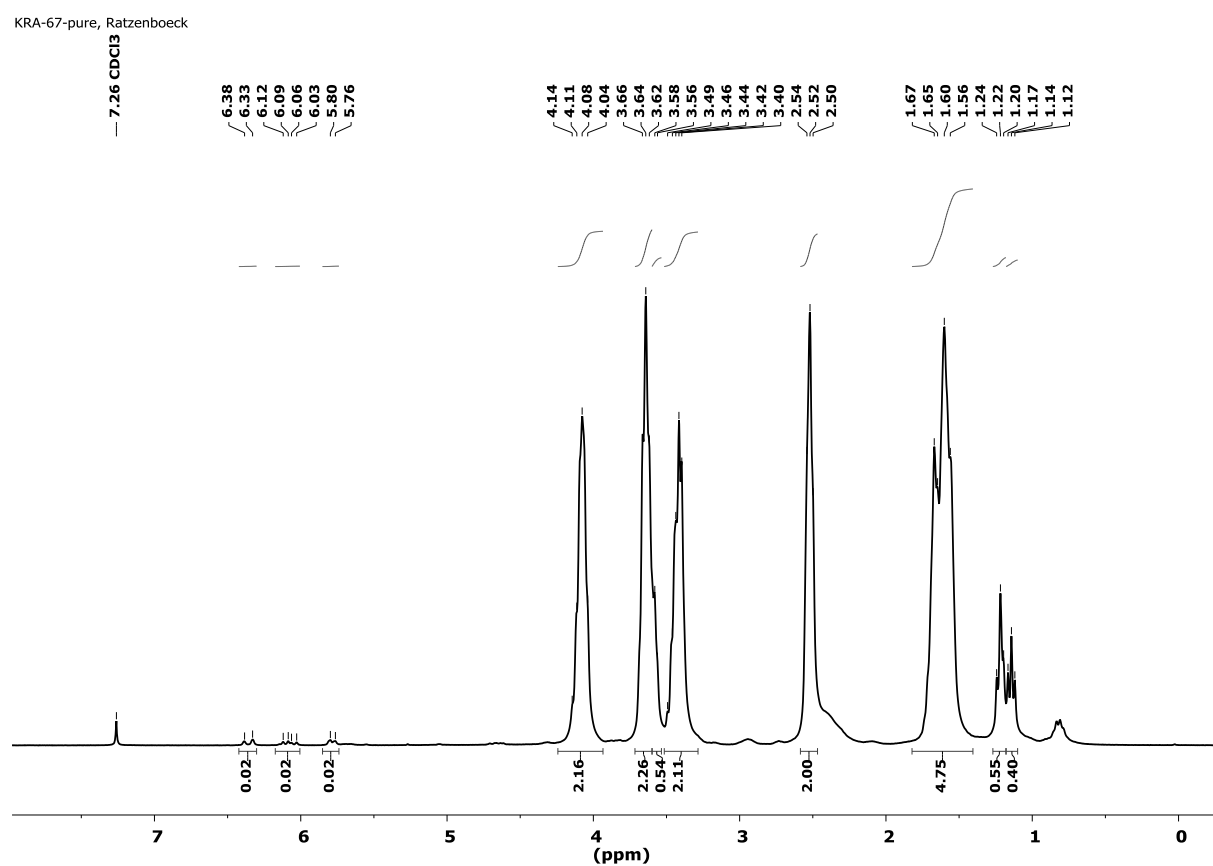


$^1\text{H-NMR}$ (300.36 MHz, CDCl_3): δ = 6.36 (d, CH, 3% end group), 6.07 (dd, CH, 3% end group), 5.79 (d, CH, 3% end group), **4.08** (t, CH_2 (1), $^3J_{\text{HH}} = 11.2$ Hz, **2.16H** and $-\text{COO-CH}_2\text{-CH}_3$, 30% end group), **3.64** (t, CH_2 (4), $^3J_{\text{HH}} = 7.1$ Hz, **2.26H**), 3.58 (t, $-\text{O-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-OH}$, 45% end group), **3.42** (t, CH_2 (5), $^3J_{\text{HH}} = 6.1$ Hz, **2.11H** and $-\text{OOC-CH}_2\text{-CH}_2\text{-O-CH}_2\text{-CH}_3$, 22% end group), **2.52** (t,

CH₂ (6), ³J_{HH} = 6.3 Hz, 2H), 1.75 – 1.45 (m, CH₂ (2 and 3), 4.75H and -O-CH₂-CH₂-CH₂-CH₂-OH, 45% end group), 1.21 (t, -COO-CH₂-CH₃, 30% end group), 1.14 (t, ³J_{HH} = 7.0 Hz, -OOC-CH₂-CH₂-O-CH₂-CH₃, 22% end group) ppm.

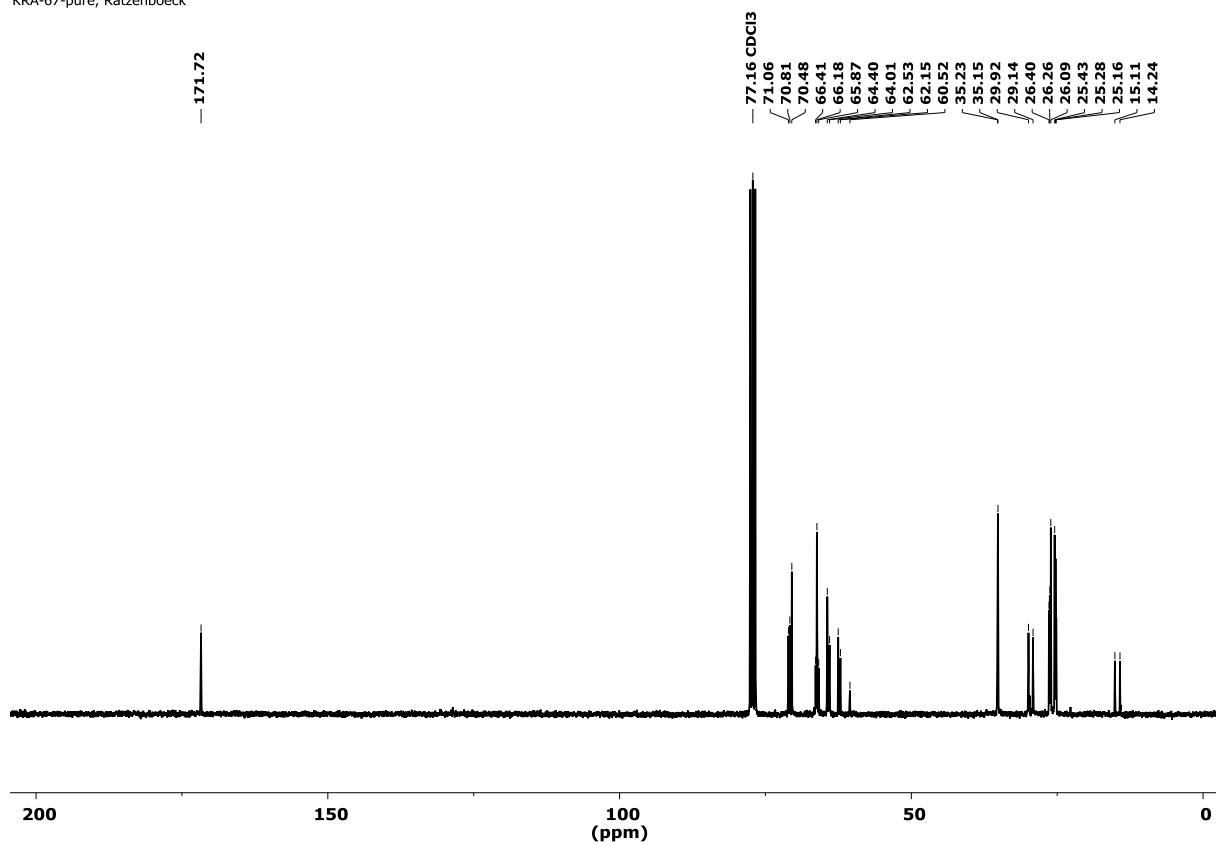
¹³C-NMR (75.53 MHz, CDCl₃): δ = 171.72 (COO), **71.06, 70.81, 70.48 (CH₂ (6)), 66.41, 66.18, 65.87 (CH₂ (4)), 64.40, 64.01 (CH₂ (1)), 62.53, 62.15 (-O-CH₂-CH₂-CH-CH₂-OH end group), 60.52 (-COO-CH₂-CH₃ end group), 35.23, 35.15 (CH₂ (5)), 29.92, 29.14, 26.40, 26.26, 26.09, 25.43, 25.28, 25.16 (CH₂ (2 and 3)), 15.11 (-OOC-CH₂-CH₂-O-CH₂-CH₃ end group), 14.24 (-COO-CH₂-CH₃ end group) ppm.**

Peaks assigned to the repeating units are printed in bold.



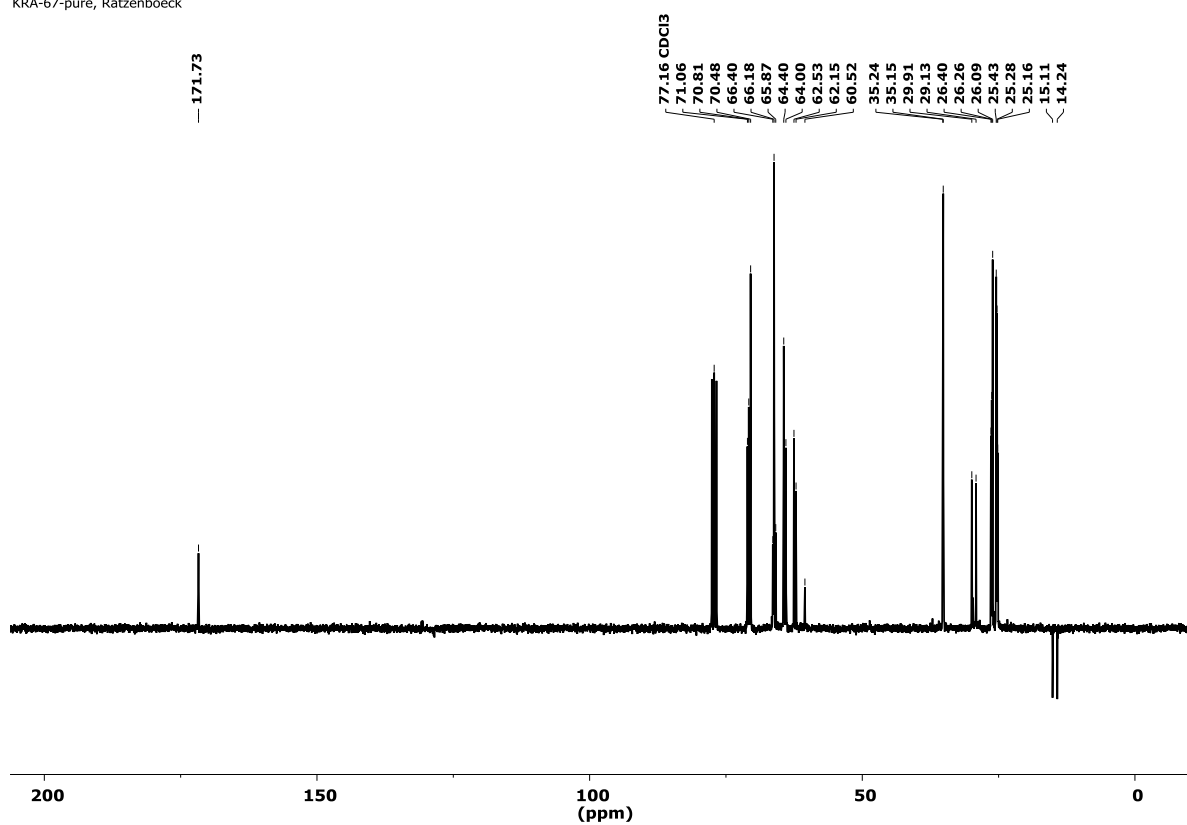
ESI Figure 20: ¹H-NMR spectrum of **poly2/7** after work-up; * denotes H grease.^[1]

KRA-67-pure, Ratzenboeck

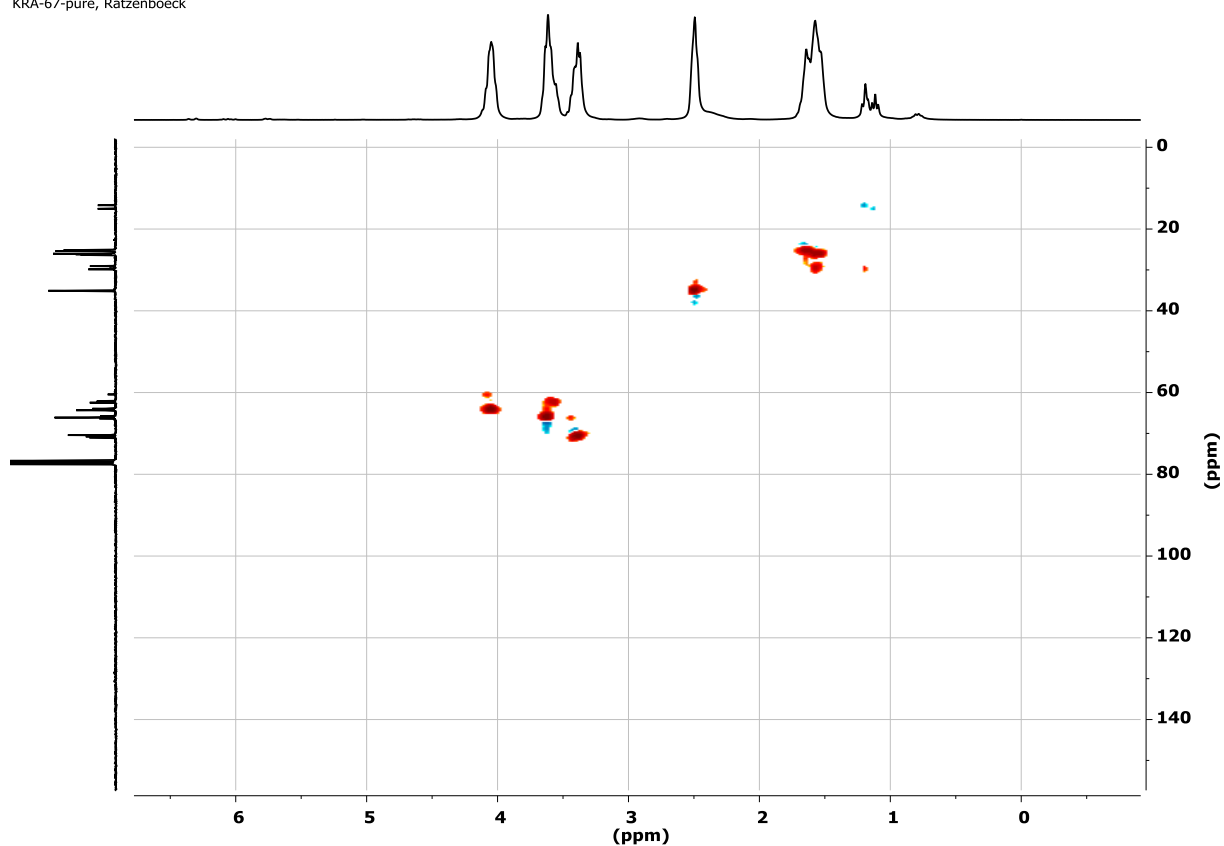


ESI Figure 21: ¹³C-NMR spectrum of **poly2/7** after work-up.

KRA-67-pure, Ratzenboeck

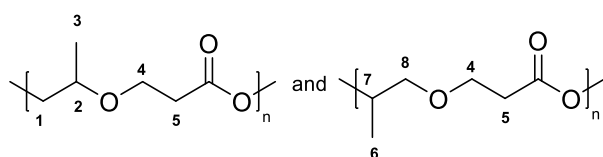


ESI Figure 22: ¹³C/APT-NMR spectrum of **poly2/7** after work-up.

ESI Figure 23: HSQC spectrum of **poly2/7** in CDCl_3 after work-up.

Preparation of **poly2/8** (according to Table 2, entry 6)

A sealed tube was charged with 174 mg (1.74 mmol, 1.00 equiv.) ethyl acrylate (**2**) and 140 mg (1.84 mmol, 1.06 equiv.) propane-1,2-diol (**8**). The reaction mixture was heated to 50 °C and 5.0 mol% (13.2 mg, 0.087 mmol) DBU was added. After 4.5 h the reaction temperature was elevated to 80 °C and the reaction tube was opened after 23 h. The reaction was further stirred for 24 h at 80 °C. After a total reaction time of 48 h the orange reaction mixture was dissolved in 5 mL CH_2Cl_2 and was extracted with 1 M HCl (1 x 5 mL). The organic layer was washed with brine (2 x 5 mL), dried over Na_2SO_4 and filtered. The solvent was removed by vacuum yielding a colorless viscous liquid.

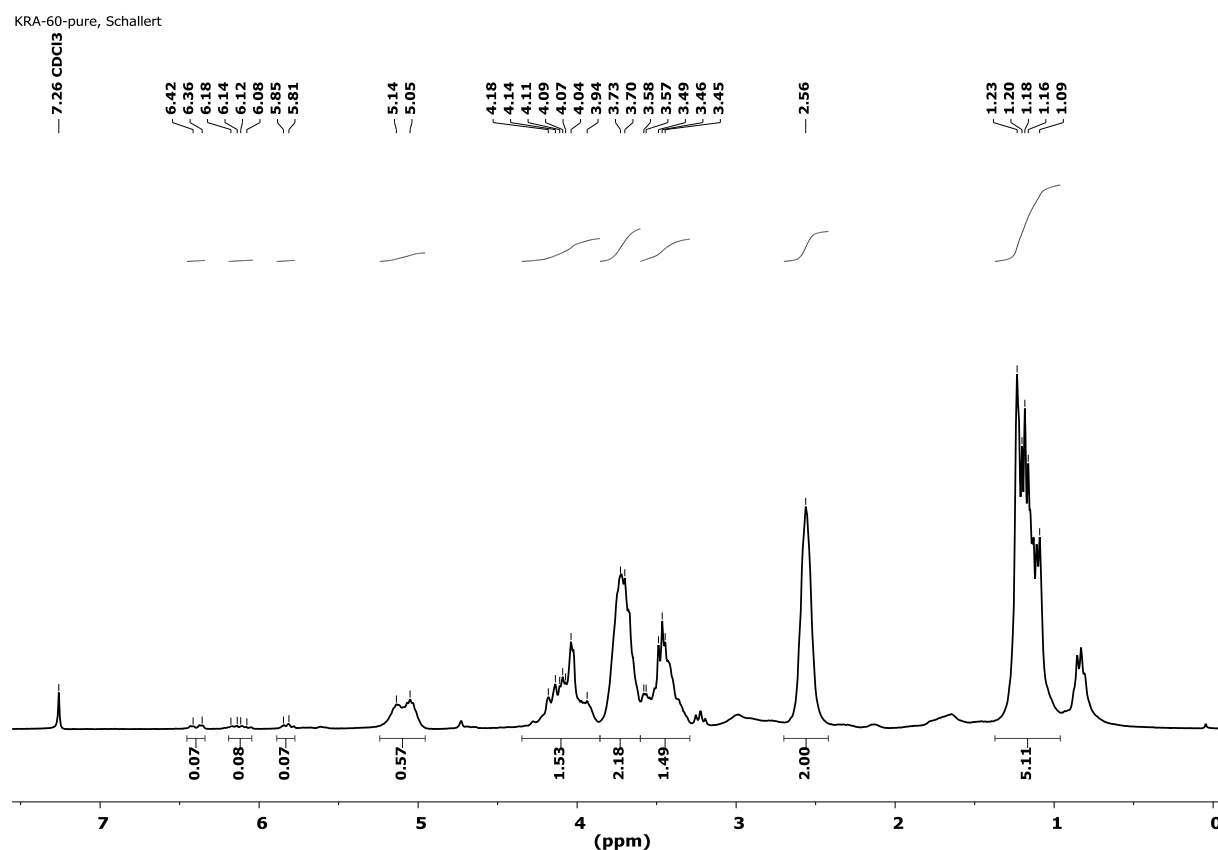


$^1\text{H-NMR}$ (300.36 MHz, CDCl_3): $\delta = 6.39$ (d, CH, $^3J_{\text{HH(E)}} = 17.2$ Hz), 6.13 (dd, CH, $^3J_{\text{HH}} = 18.4$, 11.8 Hz), 5.83 (d, CH, $^3J_{\text{HH(Z)}} = 10.3$ Hz), **5.09** (d, CH (7), **0.57H**), **4.32 – 3.87** (m, CH₂ (1), **1.53H**), **3.87 – 3.59** (m, CH₂ (4), **2.18H**), **3.54 – 3.29** (m, CH (2) and CH₂ (8), **1.49H**), **2.56** (t, CH₂ (5), **2H**), **1.46 – 0.95** (m, CH₃ (3 and 6), -OOC-CH₂-CH₂-O-CH₂-CH₃ and -COO-CH₂-CH₃ end group, **5.11H**) ppm.

$^{13}\text{C-NMR}$ (75.53 MHz, CDCl_3): $\delta = 171.46$ (COO), 74.94, **74.86, 73.74** (CH (2)), 73.39, 69.80, **69.51, 68.43** (CH (7)), **67.33, 66.74, 66.46, 66.27, 66.09, 65.85, 64.71** (CH (1 and 4 and 8)), **35.66, 35.35, 35.27** (CH₂ (5)), 32.02, 29.79, 29.46, 22.79, **19.09, 18.57, 17.18, 17.01, 16.73, 16.57, 16.23** (CH₃ (3 and 6)), 15.18 (-OOC-CH₂-CH₂-O-CH₂-CH₃ end group), 14.22 (-COO-CH₂-CH₃ end group) ppm.

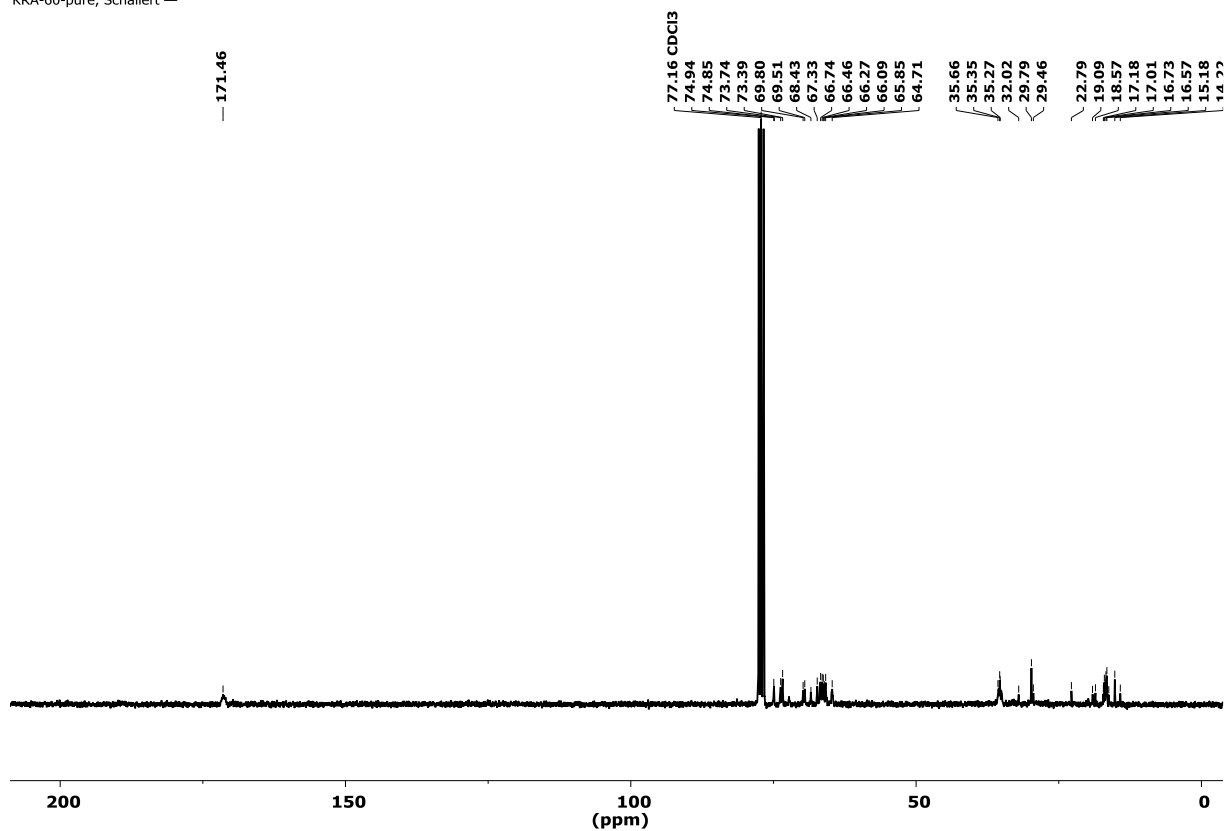
Peaks assigned to the repeating units are printed in bold.

End group distribution for **poly2/8** could not be determined by NMR spectroscopy as overlapping signals interfere with integration.



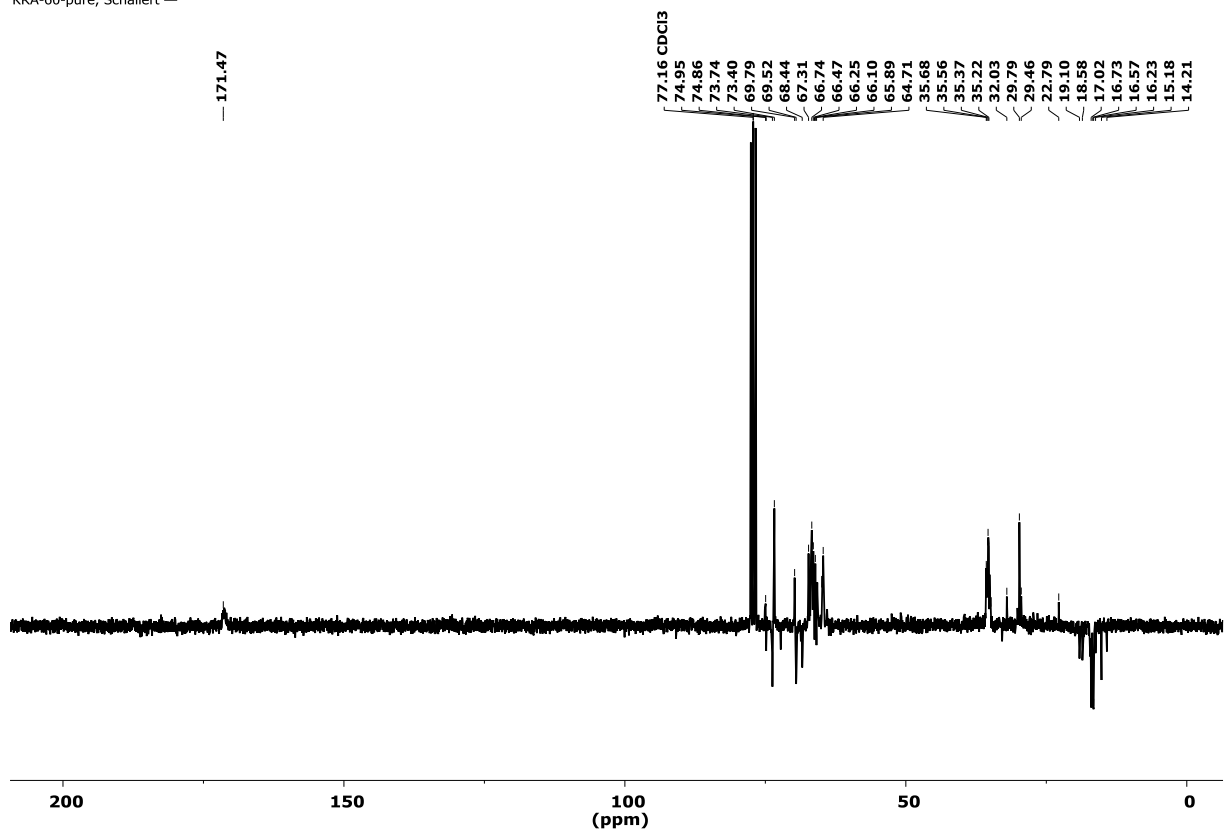
ESI Figure 24: $^1\text{H-NMR}$ spectrum of **poly2/8** after work-up; * denotes H grease.^[1]

KRA-60-pure, Schallert —

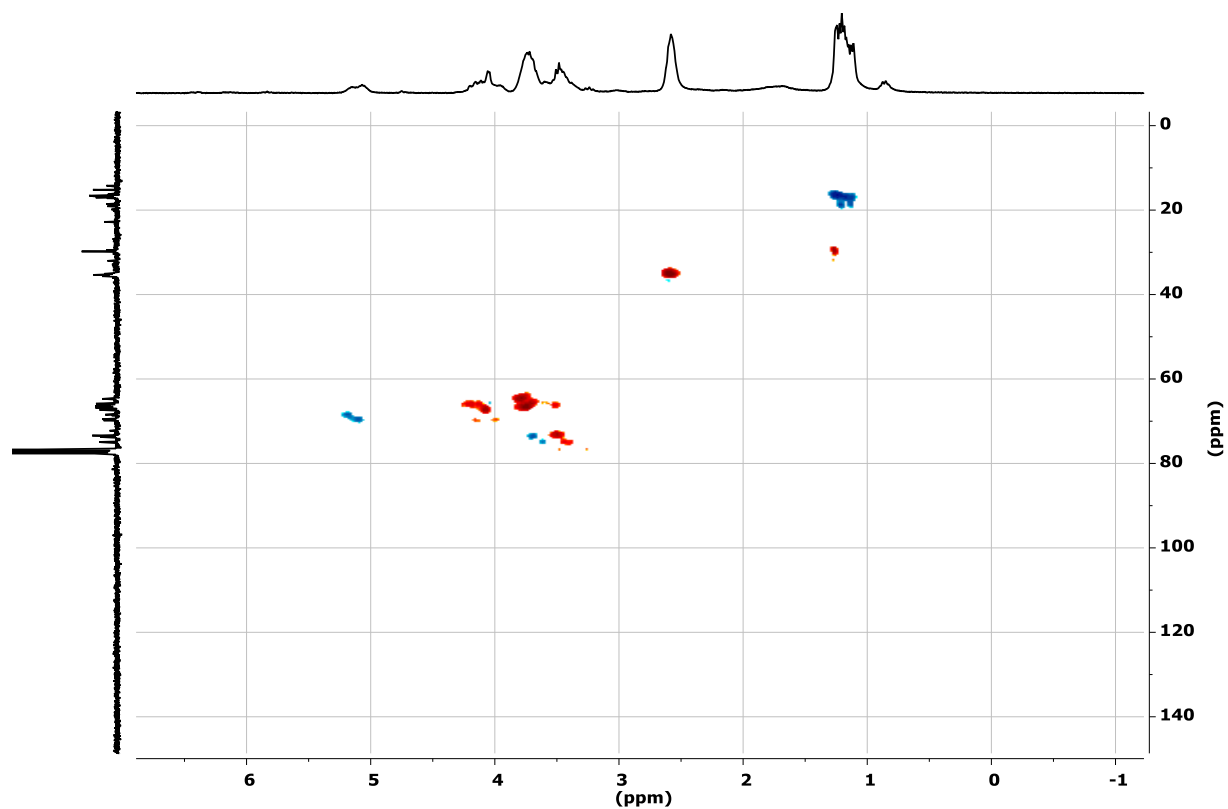


ESI Figure 25: ¹³C-NMR spectrum of **poly2/8** after work-up.

KRA-60-pure, Schallert —

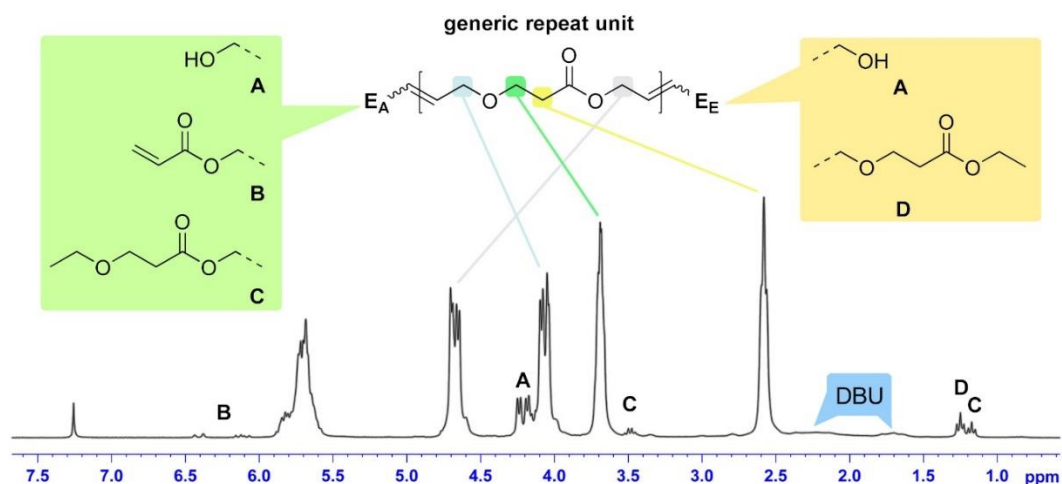


ESI Figure 26: ¹³C/APT-NMR spectrum of **poly2/8** after work-up.



ESI Figure 27: HSQC spectrum of **poly2/8** in CDCl_3 after work-up.

ESI Table 3: Calculated end group distribution based on ¹H-NMR spectroscopy for entries 1-9 in Table 1 in the main article. Method for calculation described in ESI Table 1.

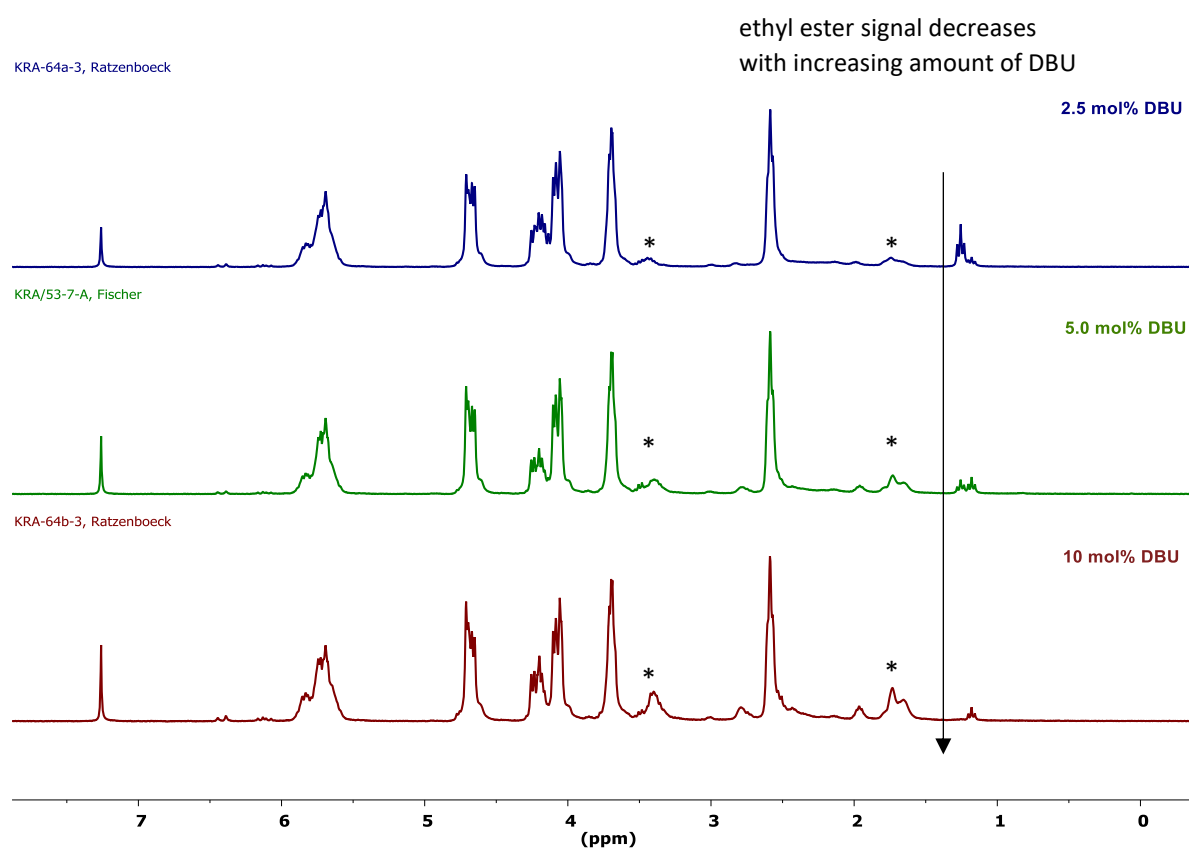


Entry		alcohol (A)	vinyl group (B)	methoxy / ethoxy-propionate (C)	methyl / ethyl ester (D)	Total number of end groups
1	Integral ¹ H-NMR	0.96	0.02	0.13	0.21	1.32
	End group distribution [%]	73	1	10	16	100
2	Integral ¹ H-NMR	0.56	0.06	0.15	0	0.77
	End group distribution [%]	72	8	20	0	100
3	Integral ¹ H-NMR	0.51	0.05	0.17	0.36	1.09
	End group distribution [%]	47	5	15	33	100
4	Integral ¹ H-NMR	0.51	0.06	0.05	0.09	0.71
	End group distribution [%]	72	8	8	12	100
6	Integral ¹ H-NMR	1.15	0.04	0.05	0.54	1.78
	End group distribution [%]	65	2	3	30	100
7	Integral ¹ H-NMR	0.85	0.04	0.07	0.21	1.16
	End group distribution [%]	73	3	6	18	100
8	Integral ¹ H-NMR	0.91	0.08	0.06	0	1.05
	End group distribution [%]	86	8	6	0	100
9	Integral ¹ H-NMR	0.95	0.07	0.06	0	1.08
	End group distribution [%]	88	6	6	0	100
10	Integral ¹ H-NMR	0.45	0	0.15	0	0.60
	End group distribution [%]	75	0	25	0	100

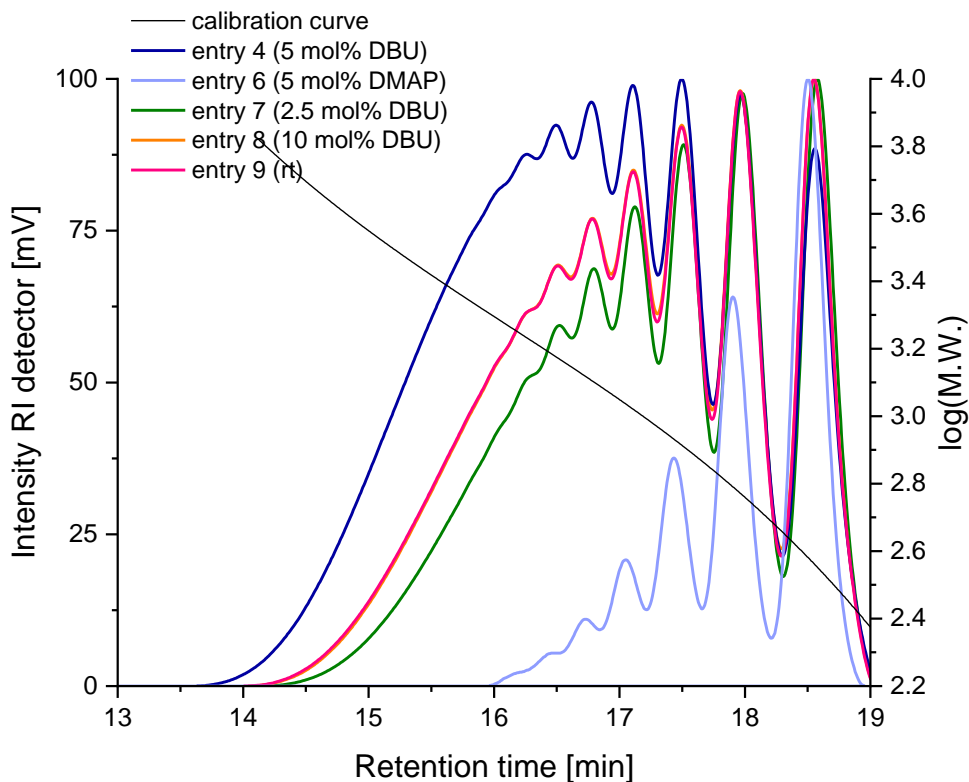
ESI Table 4: Calculated average number molecular mass based on ¹H-NMR spectroscopy for entries 1-9 in Table 1 in the main article. Method for calculation described in ESI Table 2.

Entry	One end group per oligomer	Calculated value of CH ₂ signal of the RU*	n	Molecular mass [Da] (without end groups)
1	0.66	1.87	2.8	403
2	0.387	1.847	4.8	679
3	0.543	1.833	3.4	480
4	0.355	1.947	5.5	779
6	0.888	1.953	2.2	313
7	0.582	1.933	3.3	472
8	0.525	1.940	3.7	525
9	0.540	1.940	3.6	511
10	0.298	1.853	6.2	883

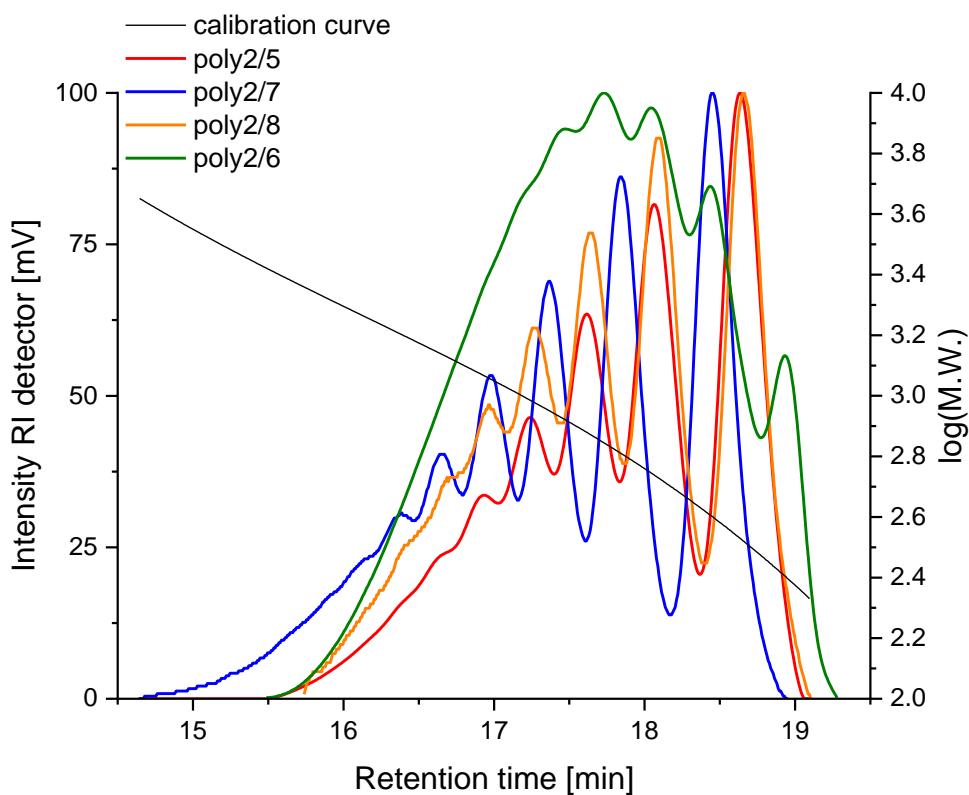
Different catalyst loadings



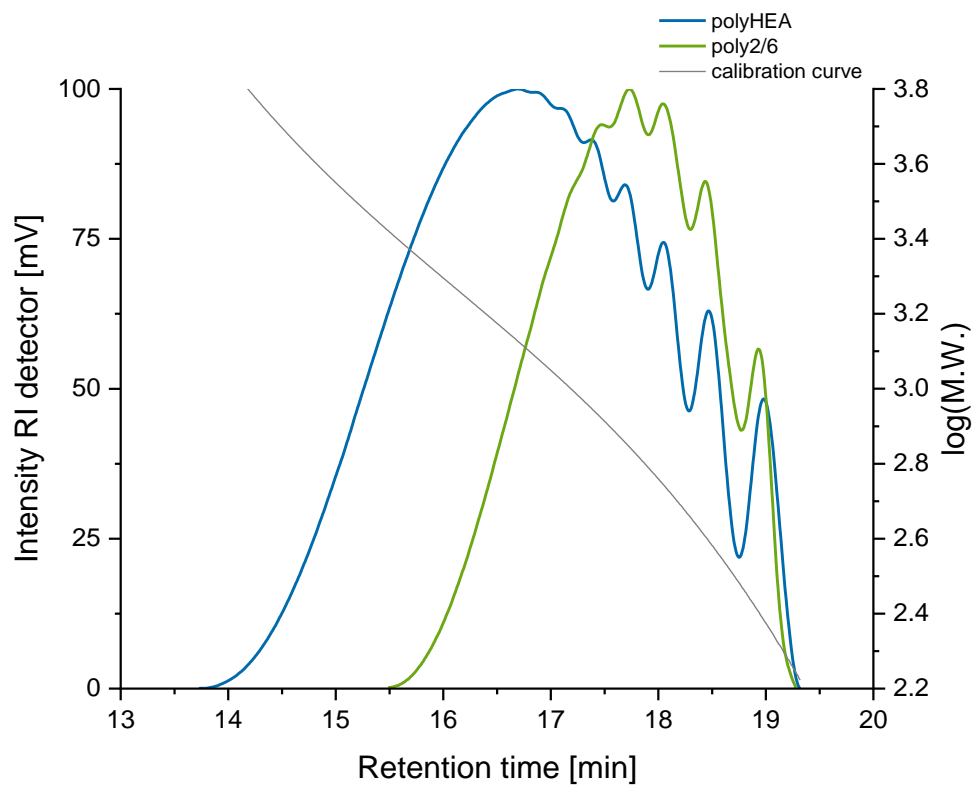
ESI Figure 28: ¹H-NMR spectra of entries 8 (10 mol%), 4 (5 mol%) and 7 (2.5 mol%) without work-up in Table 1 in the main article; * denotes DBU.



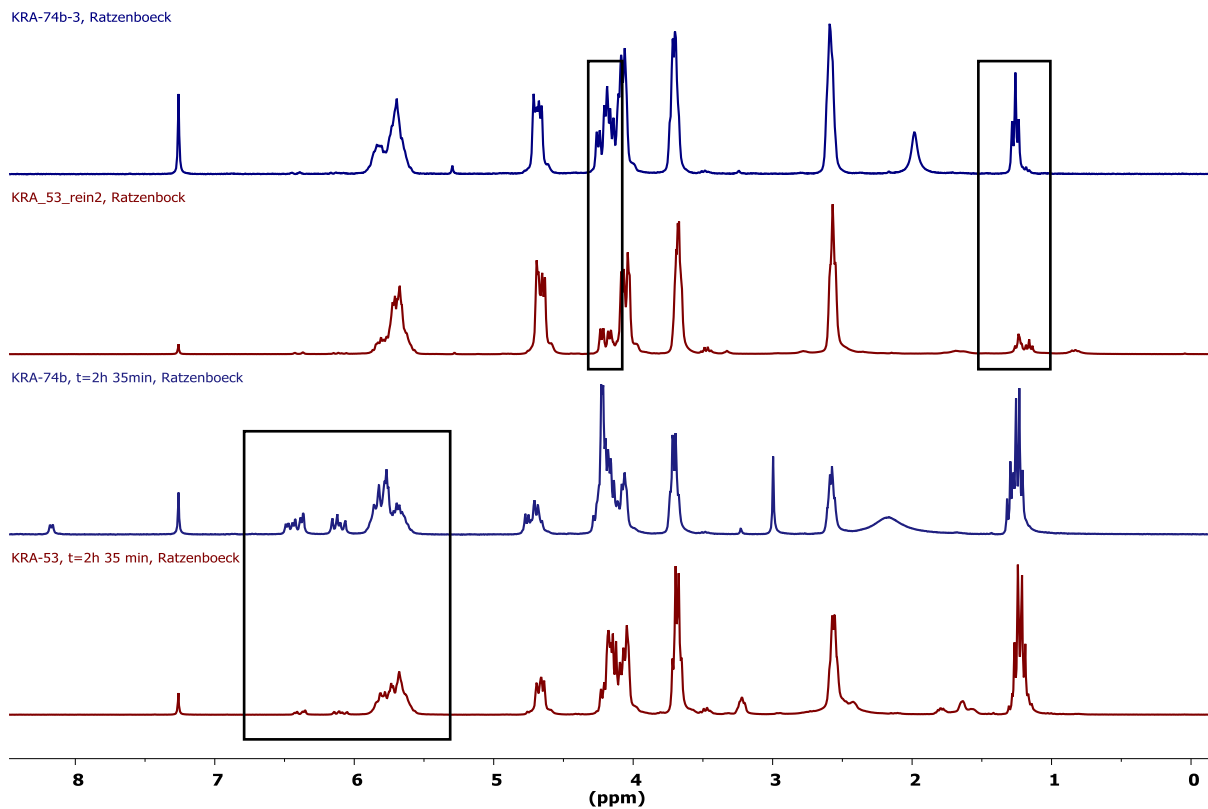
ESI Figure 29: SEC chromatograms for entries 4, 6, 7, 8 and 9 in Table 1 in the main article.



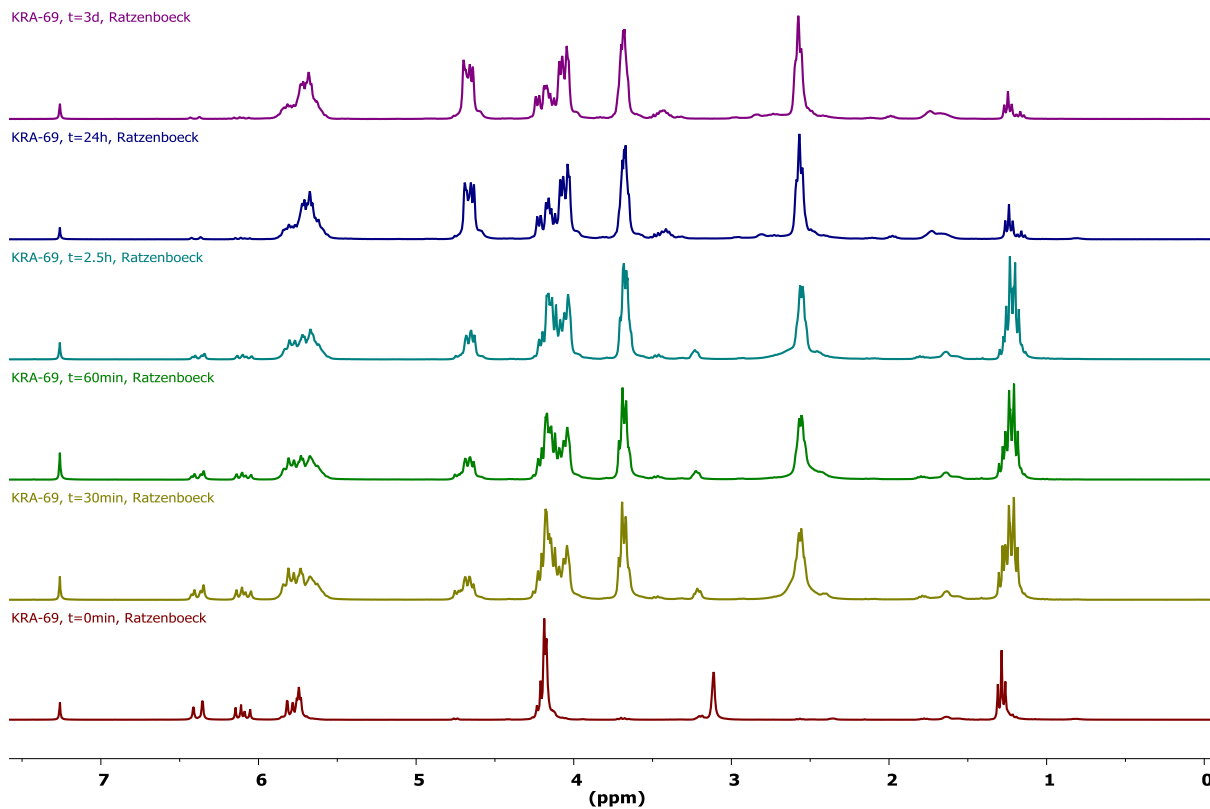
ESI Figure 30: SEC chromatograms of **poly2/5**, **poly2/6**, **poly2/7**, **poly2/8** (Table 2 in the main article, entries 3-6).



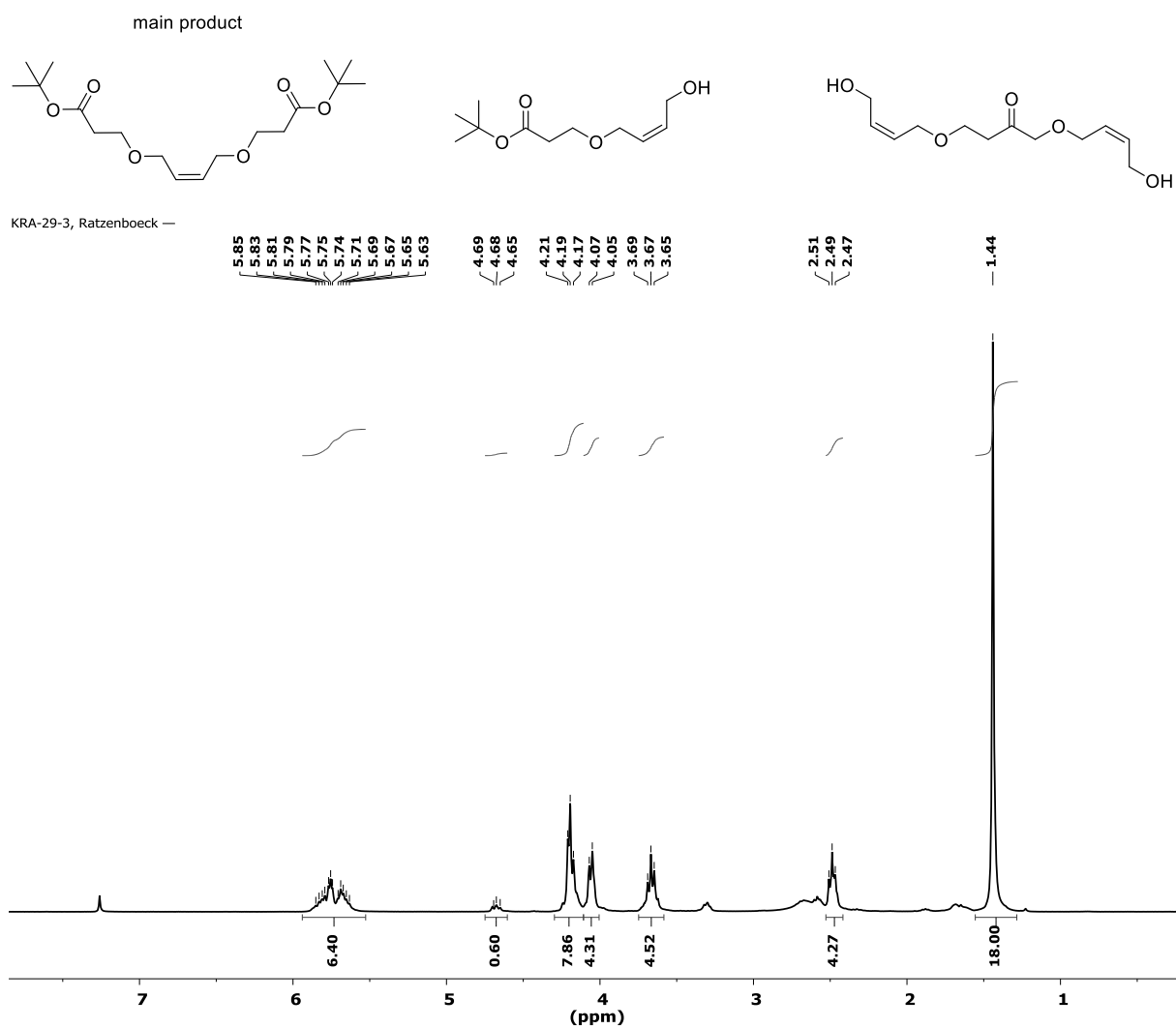
ESI Figure 31: SEC chromatograms of **poly2/6** ($M_n = 600$, $\mathcal{D} = 1.3$) and of **polyHEA** ($M_n = 880$, $\mathcal{D} = 1.7$).



ESI Figure 32: Comparison of the polymerisation of **2** and **4** according to entry 6 (blue, using DMAP) and entry 4 (red, using DBU); bottom two spectra after 2.5 h reaction time: *oxa*-Michael addition is slower in case of DMAP (see vinyl signals); upper two spectra after 24 h and work-up: ethyl ester end groups are clearly detectable in case of using DMAP.

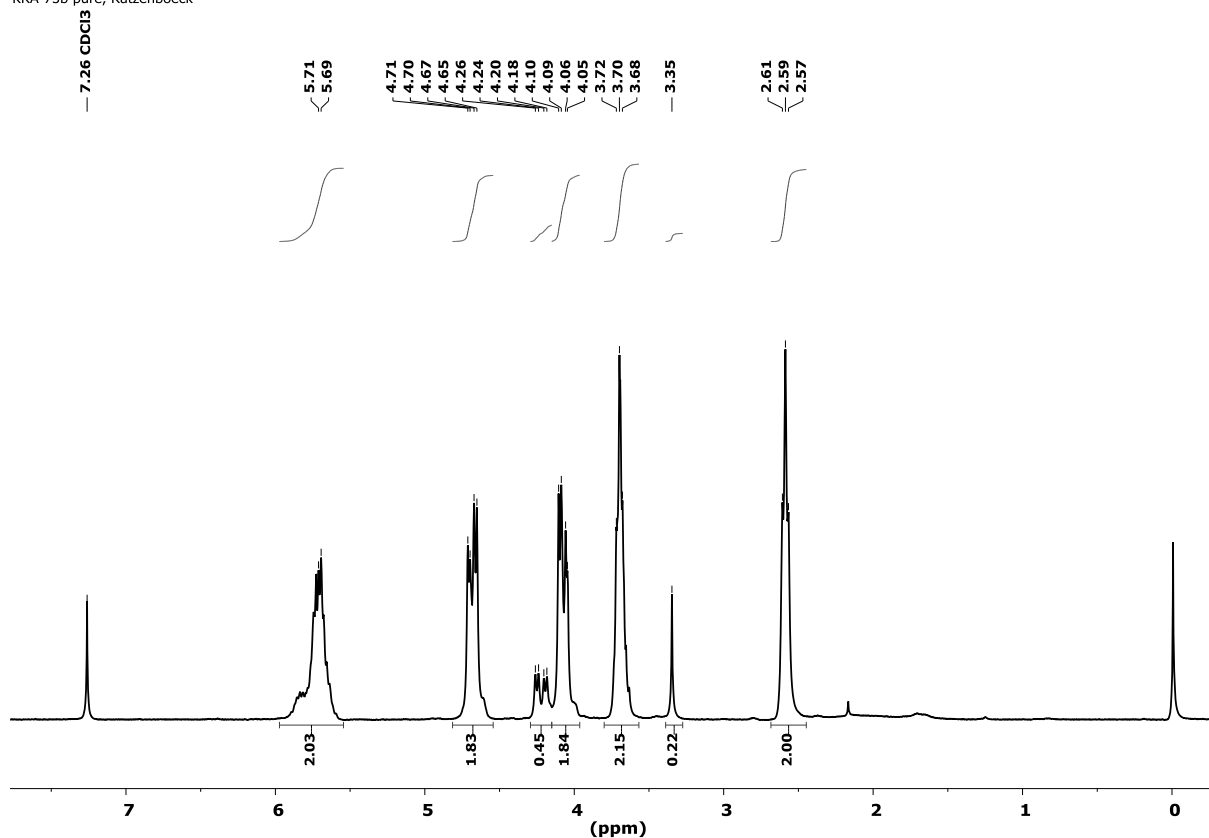


ESI Figure 33: Reaction monitoring of ethyl acrylate (**2**) and (*Z*)-2-butene-1,4-diol (**4**) with DBU via ¹H-NMR spectroscopy over 3 days.

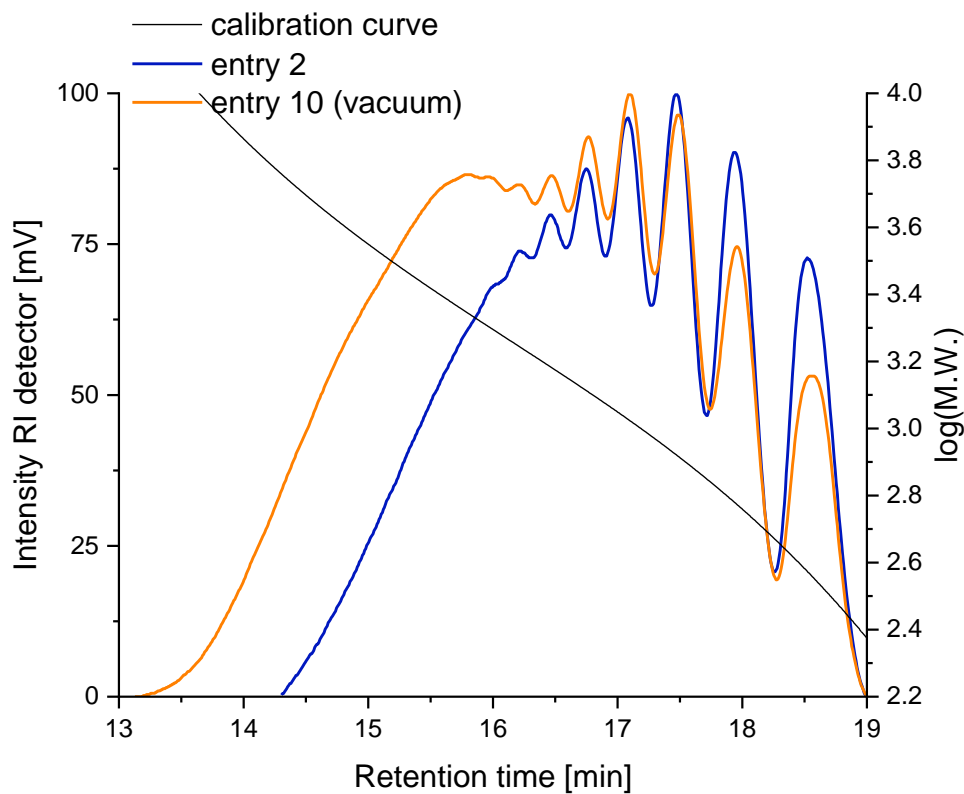


ESI Figure 34: Crude ^1H -NMR spectrum of entry 5 in Table 1 in the main article.

KRA-73b pure, Ratzenboeck —



ESI Figure 35: ¹H-NMR spectrum of optimized reaction of poly1/4 (entry 10 in Table 1 in the main article).



ESI Figure 36: SEC chromatogram of optimized reaction (vacuum) of poly1/4 (entry 10; $M_n = 1180$, $\bar{D} = 1.8$) compared to poly 1/4 (entry 2; $M_n = 910$, $\bar{D} = 1.5$).

References

- [1] G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, K. I. Goldberg, *Organometallics* **2010**, 29, 2176.