Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supplementary Information

Exploiting retro oxa-Michael chemistry in polymers

Karin Ratzenböck,[1,2] Johanna M. Uher,[1,2] Susanne M. Fischer,[1,2] David Edinger,[1,2] Viktor Schallert,[1,2] Ema Žagar,[3] David Pahovnik,[3] and Christian Slugovc [1,2,*]

[1] Institute for Chemistry and Technology of Materials, Graz University of Technology, Stremayrgasse 9, 8010 Graz, Austria; e-mail: slugovc@tugraz.at

[2] Christian Doppler Laboratory for Organocatalysis in Polymerization, Stremayrgasse 9, 8010 Graz, Austria

[3] National Institute of Chemistry, Department of Polymer Chemistry and Technology, Hajdrihova 19, 1000 Ljubljana, Slovenia

Table of Contents

1. General Information

All experiments were performed under ambient conditions. Chemicals purchased from Alfa Aesar, Sigma Aldrich or TCI were used as received.

NMR spectroscopy: ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer (^{1}H: 300.36 MHz; ^{13}C: 75.53 MHz), a Bruker Avance NEO 400 MHz spectrometer (^{1}H: 400.14 MHz) or a Varian Inova 500 MHz instrument (^{1}H: 499.84 MHz) at 25 °C. Chemical shifts δ are given in ppm relative to residual protons and carbon signals of the deuterated solvent.

Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) measurements were performed using a Bruker UltrafleXtreme MALDI-TOF mass spectrometer (Bruker Daltonik). Samples were dissolved in chloroform (10 mg mL^{-1}) and mixed with a solution of matrix, dithranol in chloroform (30 mg mL^{-1}), and potassium trifluoroacetate in THF (10 mg mL^{-1}), at a volume ratio of 1:10:3. The solution (0.6 µL) was spotted onto the target plate (dried-droplet method). The reflective positive ion mode was used to record the mass spectra of the samples. Calibration was done externally with the poly(methyl methacrylate) standards (MALDI validation set PMMA, Fluka Analytical) using the nearest-neighbor position method.

Size exclusion chromatography (SEC) was carried out on a system provided by Shimadzu equipped with two separating columns, a UV detector (SPD-20A) and RI detector (RID-20A) using THF or chloroform as eluent. Samples (of **poly 3**) were analyzed in THF with two separating columns MZ-Gel SDplus 500 Å 5µm 300x8mm and MZ-Gel SDplus 100 Å 5 µm 300x8 mm. Samples (of **poly 1**) in chloroform were analyzed with two separating columns MZ-Gel SDplus linear 5µm 300x8 mm.

The molar mass characteristics of **poly 2** samples were determined by size-exclusion chromatography coupled with an Optilab differential Refractive Index detector (RI, Wyatt Technology Corporation, USA). Separations of samples were performed at RT in chloroform ($CHCl_3$; purity 99.8%, Honeywell, USA) using an Agilent 1260 HPLC chromatograph (Agilent Technologies, USA) and an OligoPore (7.5 300 mm, 6 µm) analytical column with a precolumn (Agilent Technologies, USA)). The nominal flow rate of the eluent was 0.8 mL min^{-1}. The OligoPore column was calibrated with poly(styrene) standards (Agilent Technologies, USA) with narrow molar mass distribution and dissolved in chloroform. The concentrations of the samples and standards were typically 10 mg mL^{-1}, while the corresponding injected masses on

the column were typically 1 mg. Astra 8.0.1.21 software with conventional calibration module (Wyatt Technology Corporation, USA) was used for data acquisition and evaluation.

IR spectra were recorded on a Bruker ALPHA FT-IR spectrometer from 4000-400 cm^{-1} with a resolution of 2 cm^{-1} and a sample scan time of 24 scans per spectrum.

Thermogravimetric analysis (TGA) was performed with a Netzsch simultaneous thermal analyzer STA 449C (crucibles: aluminum from Netzsch). The heating rate was 10 °C/min until a final temperature of 550 °C was reached. A helium flow of 20 $mL \cdot min^{-1}$ was used in combination with a protective flow of helium of 10 $mL \cdot min^{-1}$.

Differential scanning calorimetry (DSC) measurements were performed on a PerkinElmer DSC 8500 instrument using aluminum sealed pans. A temperature range from -40 to 140 °C with a heating and cooling rate of 20 °C/min for the first and second run and 40 °C/min for the third run was chosen.

Stress relaxation experiments were performed on an Anton Paar MCR 502 rheometer using a parallel plate setup with a diameter of 8 mm. The lower plate was heated to the respective temperature and the sample was placed on it. A normal force of 1 N was preset before applying a strain of 1%. The decline of the relaxation modulus ($G_{(t)}$) was monitored over time at 170, 180, 190 and 200 °C giving the respective relaxation time (τ^*). τ^* is defined as the time at which $G_{(t)}/G_0 = 1/e$. τ^* was determined three times for each temperature and the natural logarithm of τ^* was plotted against 1000 divided by the respective temperature. The flow activation energy was calculated from the linear fit of this plot according to the following equation:

$$\ln(\tau^*) = \frac{E_a}{R} * \frac{1000}{T} - \ln(A)$$

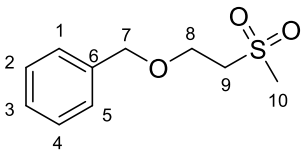
The effect of reprocessing on the viscoelastic behaviour was simulated by reapplying the same sample several times and letting it cool down to room temperature after every measurement. Stress relaxation experiments on reprocessed material were conducted at 180°C. Frequency sweep experiments were conducted at the same temperature at a given strain of 1% in a frequency range from 0.1 to 100 rad/s.

2. Synthesis oxa-Michael adducts

General reaction procedure oxa-Michael addition of vinyl sulfones:

In a 4 mL reaction vessel the catalyst KOH (5 mol%) was dissolved in the respective alcohol (1.05 equiv.). Thereafter, methyl vinyl sulfone (MVS) (1.00 equiv.) was added and the reaction was stirred at room temperature overnight. Full conversion to the product was confirmed by ^{1}H-NMR spectroscopy. In the following, the reaction mixture was diluted with methylene chloride and the organic layer was extracted with 1 M HCl. The organic layer was further washed twice with brine, dried over Na_2SO_4 and filtered. The solvent was removed by vacuum yielding light yellow to orange liquids.

((2-(Methylsulfonyl)ethoxy)methyl)benzene (1)



1.00 g (9.42 mmol, 1.00 equiv.) methyl vinyl sulfone, 1.02 g (9.45 mmol, 1.00 equiv.), 5.7 mol% (30.1 mg, 0.536 mmol) KOH

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.33 (m, H-1, H-2, H-3, H-4, H-5, 5H), 4.56 (s, H-7, 2H), 3.93 (t, H-8, 2H), 3.24 (t, H-9, 2H), 2.99 (s, H-10, 3H) ppm.

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 137.1 (C-6), 128.8 (C-2, C-4), 128.3 (C-3), 128.0 (C-1, C-5), 73.8 (C-7), 64.3 (C-8), 55.6 (C-9), 43.3 (C-10) ppm.

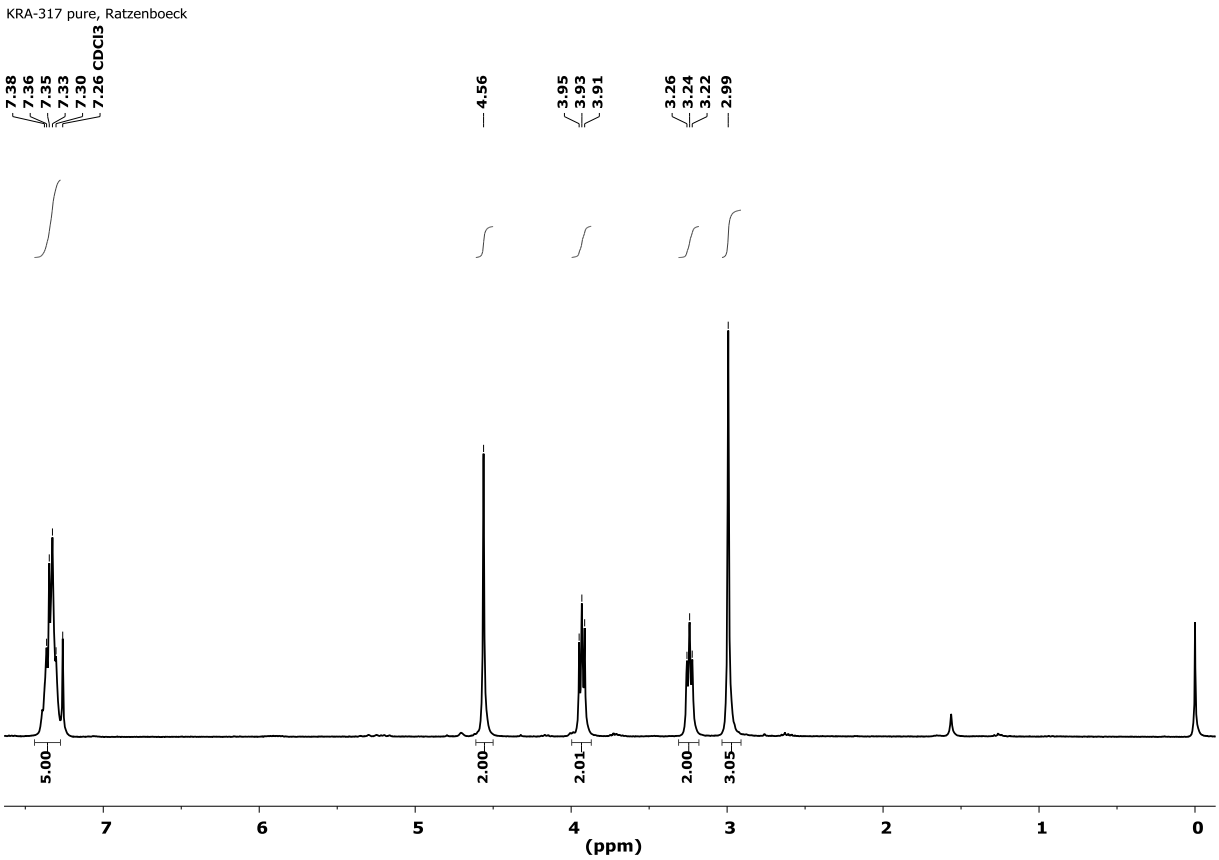


Figure S1. ^{1}H-NMR spectrum of **1** in $CDCl_3$.

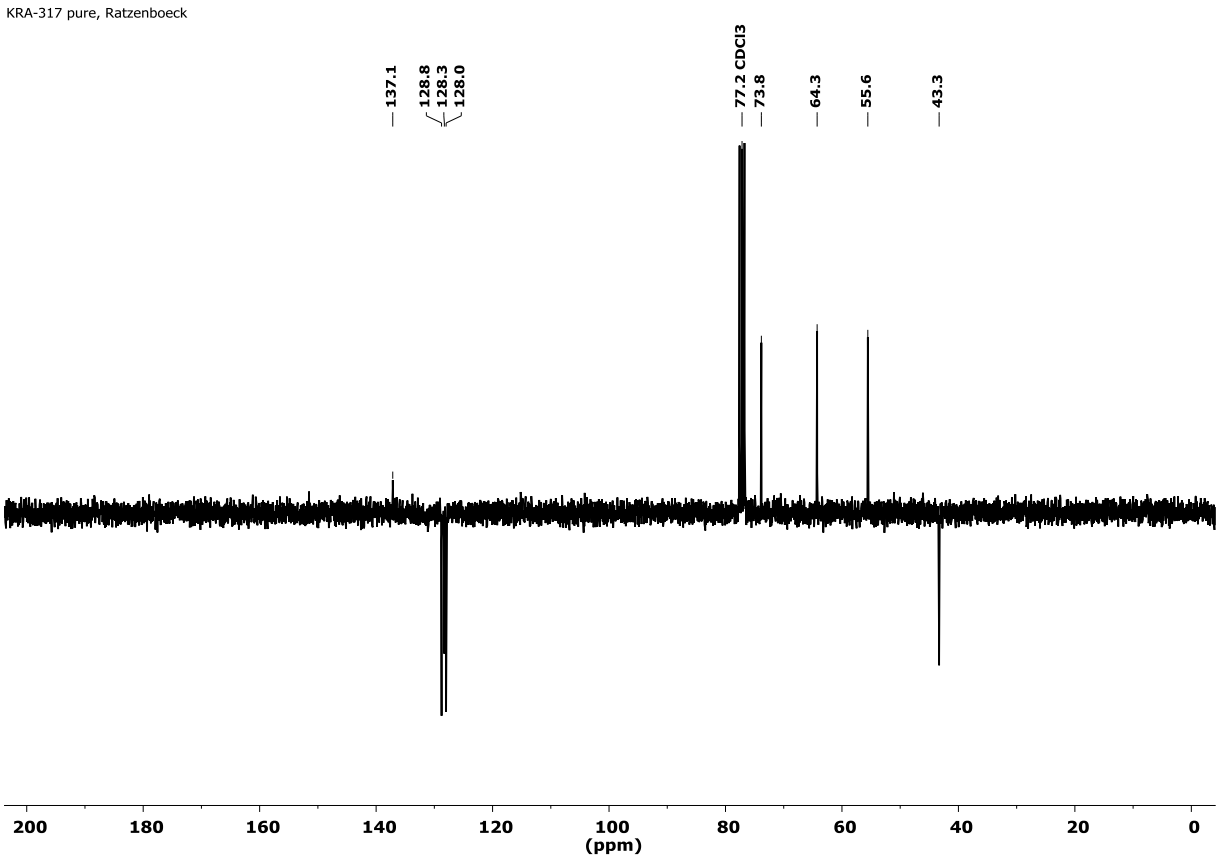
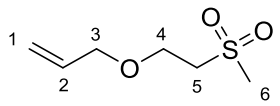


Figure S2. ^{13}C/APT-NMR spectrum of **1** in $CDCl_3$.

3-(2-(Methylsulfonyl)ethoxy)prop-1-ene (2)



427 mg (4.03 mmol, 1.00 equiv.) methyl vinyl sulfone, 246 mg (4.23 mmol, 1.05 equiv.) allyl alcohol, 4.5 mol% (10.2 mg, 0.182 mmol) KOH

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 5.95 – 5.82 (m, H-2, 1H), 5.31 – 5.20 (m, H-1, 2H), 4.03 (d, H-3, 2H), 3.88 (t, H-4, 2H), 3.22 (t, H-5, 2H), 3.00 (s, H-6, 3H) ppm.

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 133.7 (C-2), 118.0 (C-1), 72.5 (C-3), 64.0 (C-4), 55.5 (C-5), 43.3 (C-6) ppm.

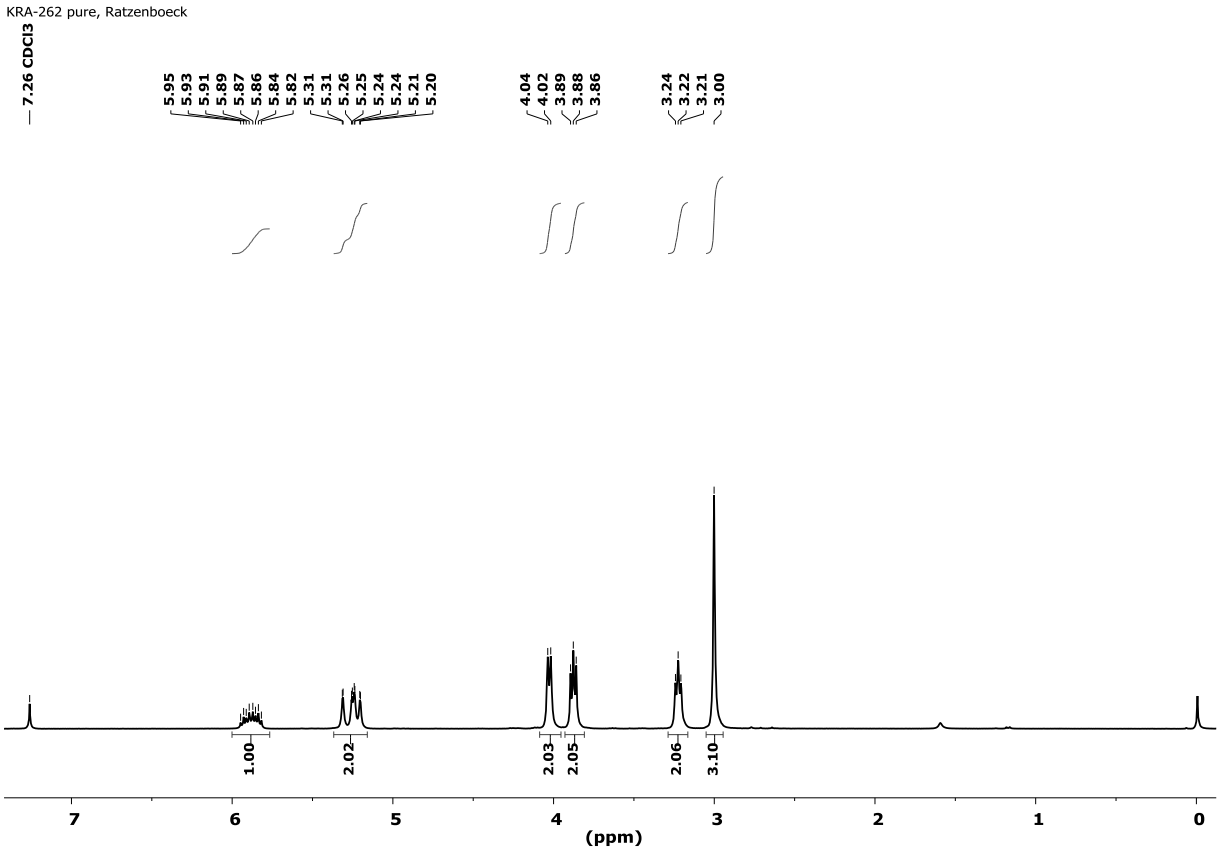


Figure S3. ^{1}H-NMR spectrum of **2** in $CDCl_3$.

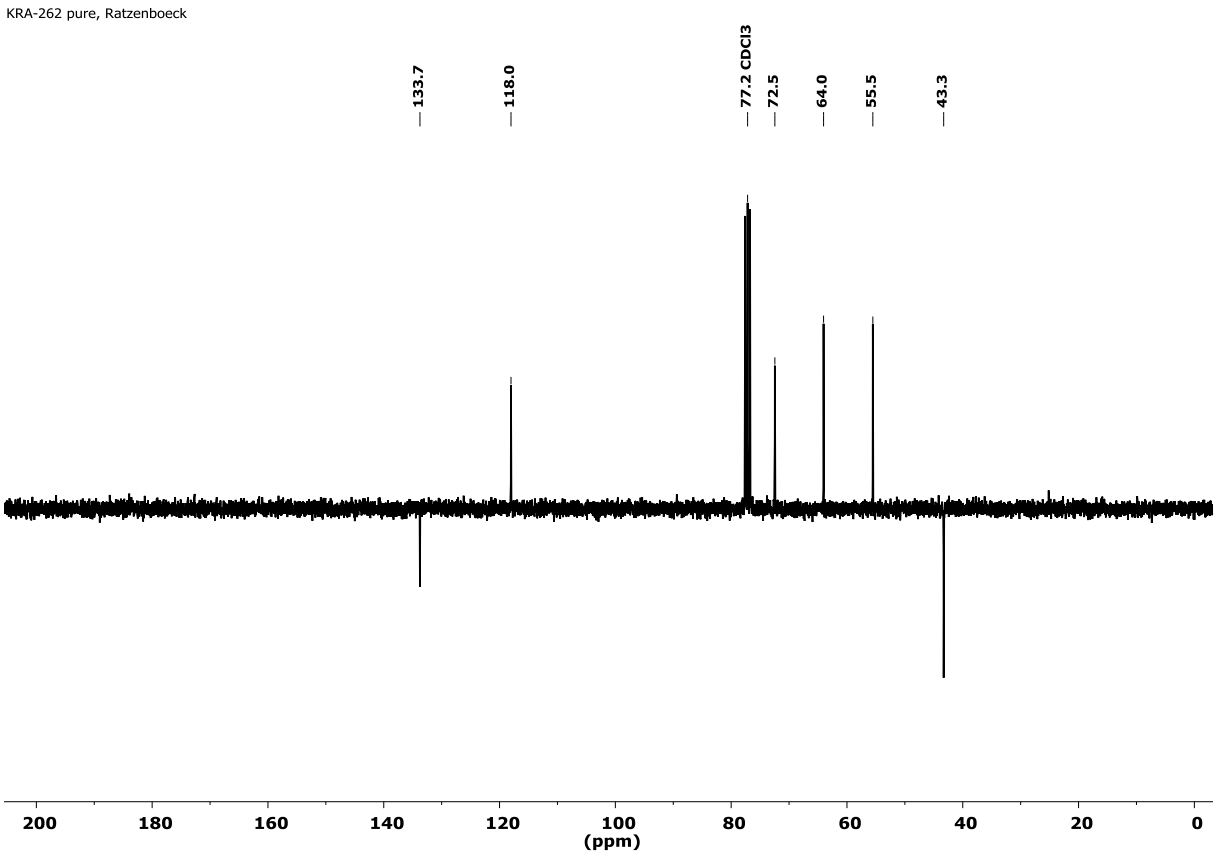
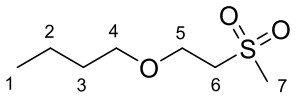


Figure S4. ^{13}C/APT-NMR spectrum of **2** in $CDCl_3$.

1-(2-(Methylsulfonyl)ethoxy)butane (3)



293 mg (2.76 mmol, 1.00 equiv.) methyl vinyl sulfone, 215 mg (2.89 mmol, 1.05 equiv.) butanol, 5.3 mol% (8.2 mg, 0.15 mmol) KOH

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 3.84 (t, H-5, 2H), 3.47 (t, H-4, 2H), 3.20 (t, H-6, 2H), 2.99 (s, H-7, 3H), 1.60 – 1.51 (m, H-3, 2H), 1.42 – 1.29 (m, H-2, 2H), 0.92 (t, H-1, 3H) ppm.

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 71.5 (C-4), 64.6 (C-5), 55.6 (C-6), 43.2 (C-7), 31.7 (C-3), 19.5 (C-2), 14.0 (C-1) ppm.

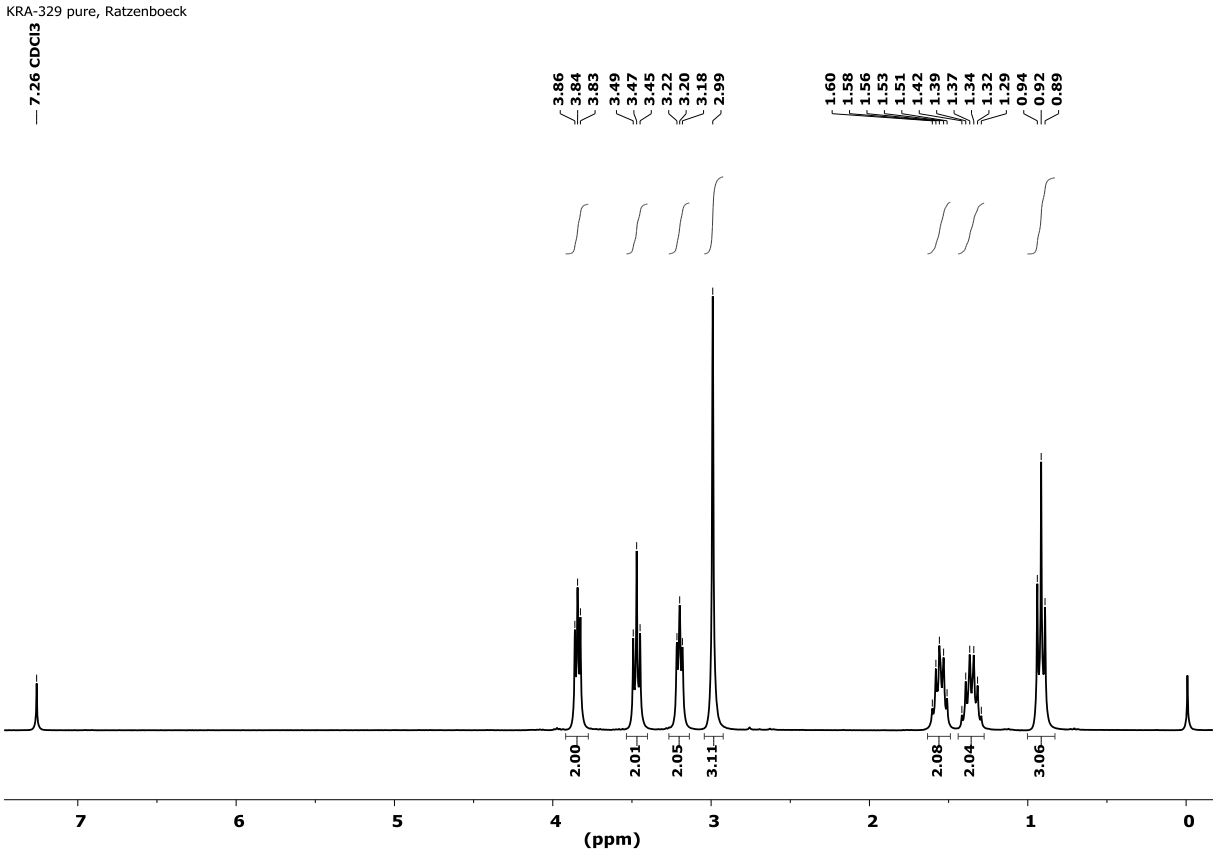


Figure S5. ^{1}H-NMR spectrum of **3** in $CDCl_3$.

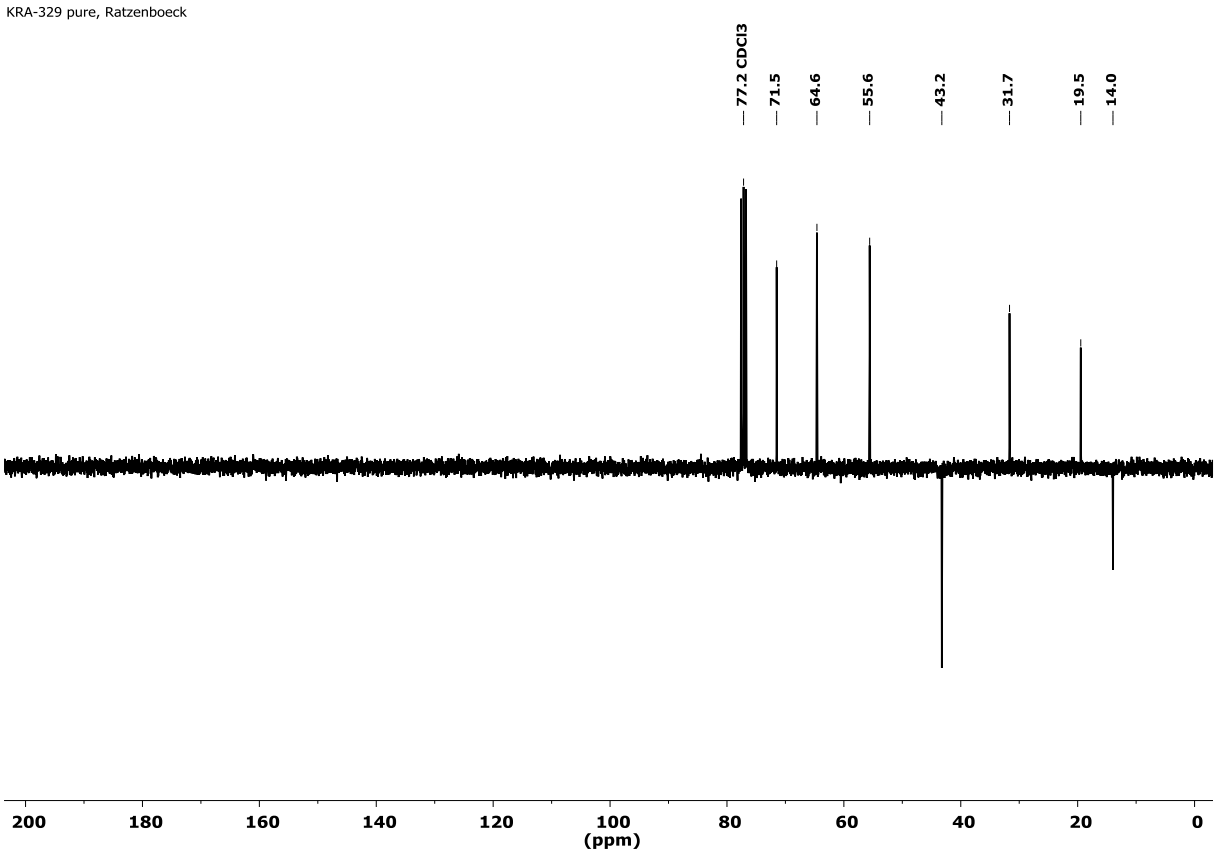
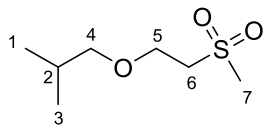


Figure S6. ^{13}C/APT-NMR spectrum of **3** in $CDCl_3$.

2-Methyl-1-(2-(methylsulfonyl)ethoxy)propane (4)



304 mg (2.86 mmol, 1.00 equiv.) methyl vinyl sulfone, 218 mg (2.94 mmol, 1.03 equiv.) isobutanol, 5.2 mol% (8.3 mg, 0.15 mmol) KOH

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 3.84 (t, H-5, 2H), 3.24 (d, H-4, 2H), 3.21 (t, H-6, 2H), 3.00 (s, H-7, 3H), 1.87 (m, H-2, 1H), 0.90 (d, H-1, H-3, 6H) ppm.

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 78.6 (C-4), 64.8 (C-5), 55.6 (C-6), 43.2 (C-7), 28.5 (C-2), 19.5 (C-1, C-3) ppm.

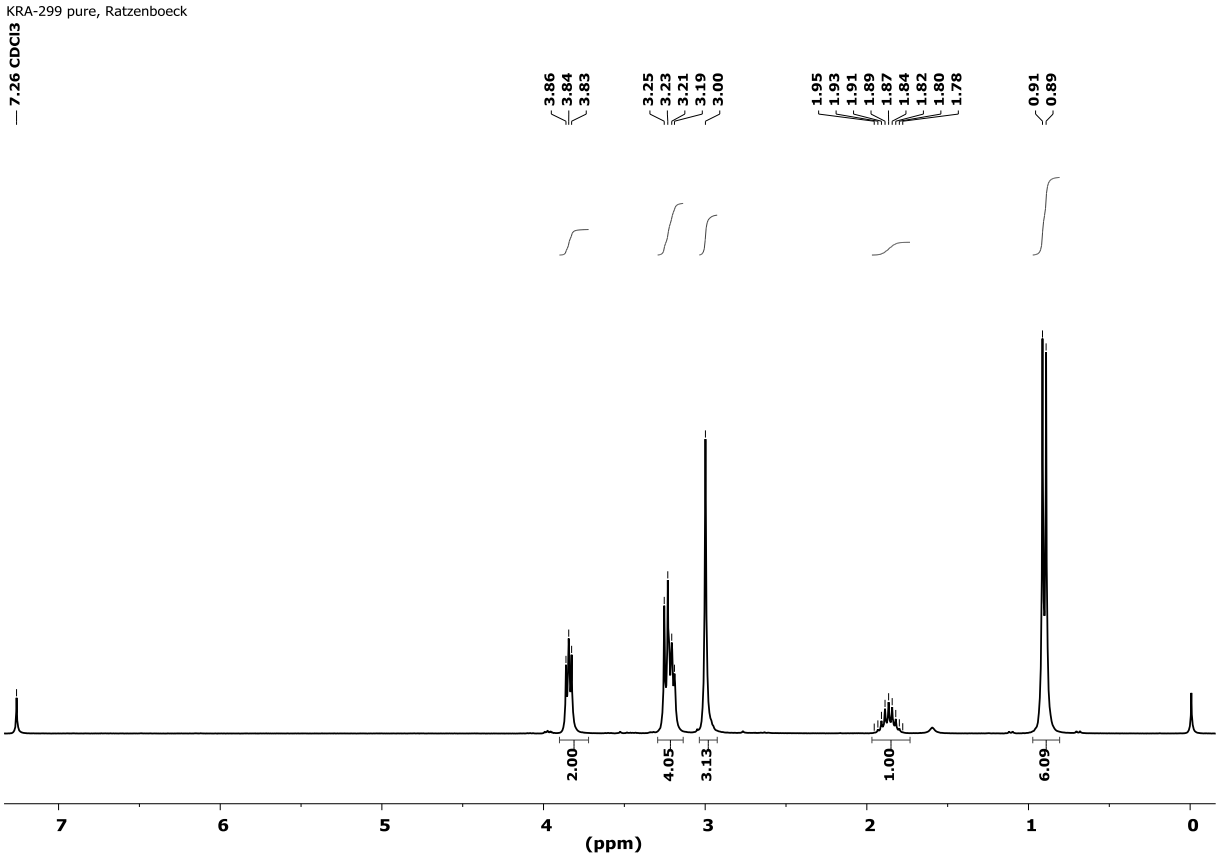


Figure S7. ^{1}H-NMR spectrum of **4** in $CDCl_3$.

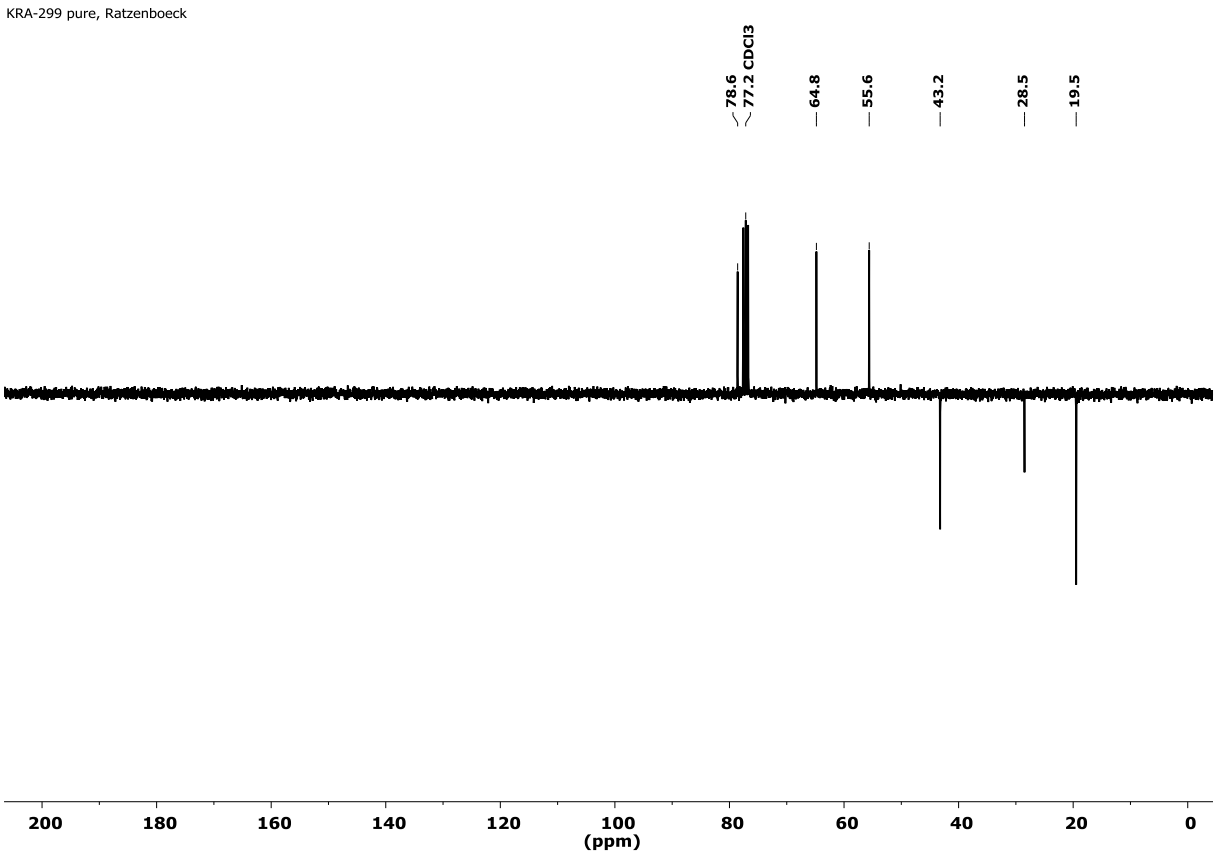
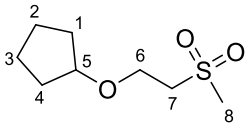


Figure S8. ^{13}C/APT-NMR spectrum of **4** in $CDCl_3$.

(2-(Methylsulfonyl)ethoxy)cyclopentane (5)



332 mg (3.13 mmol, 1.00 equiv.) methyl vinyl sulfone, 271 mg (3.15 mmol, 1.01 equiv.) cyclopentanol, 4.2 mol% (7.4 mg, 0.13 mmol) KOH

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 3.94 (s, H-5, 1H), 3.81 (t, H-6, 2H), 3.18 (t, H-7, 2H), 2.98 (s, H-8, 3H), 1.74 – 1.55 (m, H-1, H-2, H-3, H-4, 8H) ppm.

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 82.4 (C-5), 62.6 (C-7), 55.8 (C-6), 43.4 (C-8), 32.2 (C-1, C-4), 23.7 (C-2, C-3) ppm.

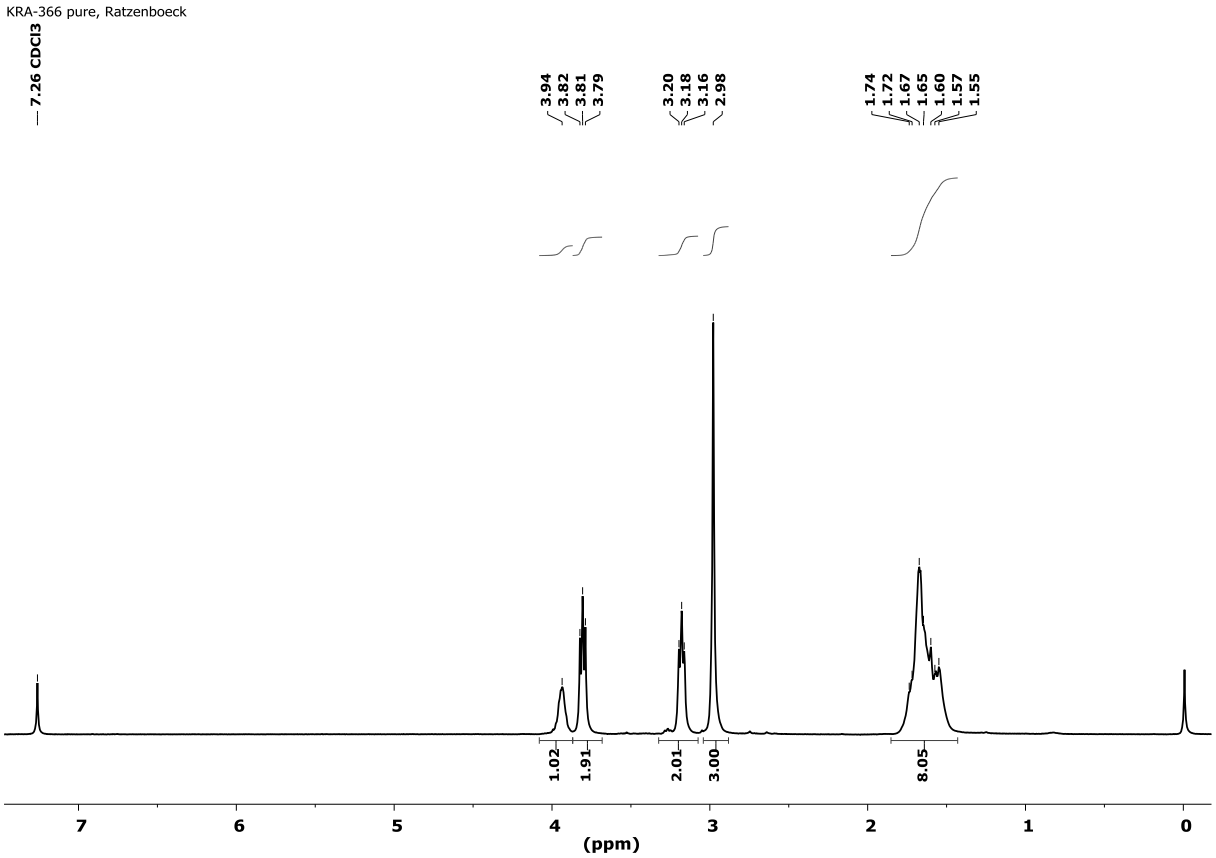


Figure S9. ^{1}H-NMR spectrum of **5** in $CDCl_3$.

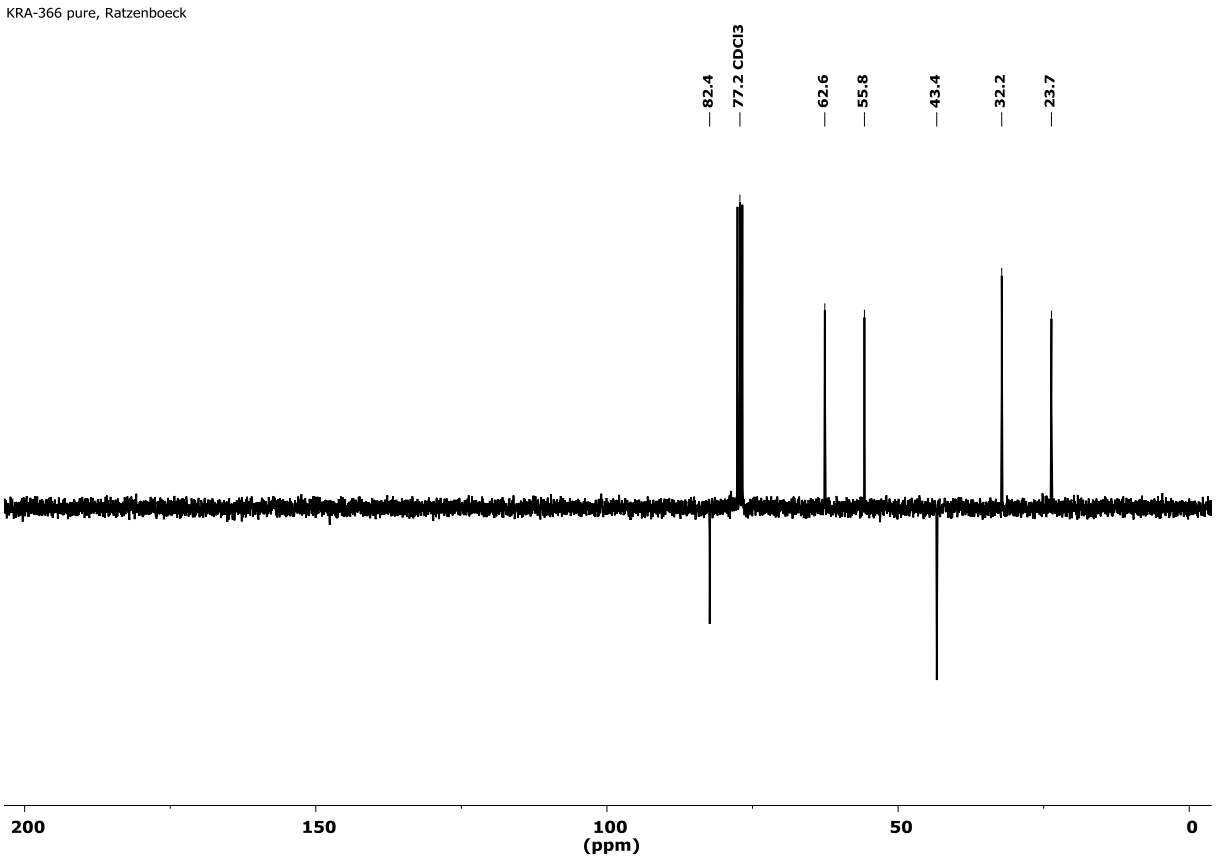
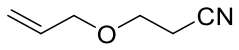


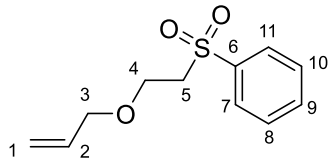
Figure S10. ^{13}C/APT-NMR spectrum of **5** in $CDCl_3$.

3-(Allyloxy)propanenitrile (7)



In a 4 mL reaction vessel 3.8 mol% (10.3 mg, 0.184 mmol) KOH was dissolved in 381 mg (6.56 mmol, 1.4 equiv.) allyl alcohol. Thereafter, 255 mg (4.80 mmol, 1.00 equiv.) acrylonitrile was added and the reaction was stirred overnight at room temperature leading to full conversion. Excess of allyl alcohol was removed in vacuumm. ^{1}H-NMR data is in accordance with literature.[1]

((2-(Allyloxy)ethyl)sulfonyl)benzene (8)



((2-(Allyloxy)ethyl)sulfonyl)benzene (**8**) was synthesized as described in "General reaction procedure oxa-Michael addition of vinyl sulfones".

334 mg (1.99 mmol, 1.00 equiv.) phenyl vinyl sulfone, 117 mg (2.02 mmol, 1.02 equiv.) allyl alcohol, 5.3 mol% (5.9 mg, 0.11 mmol) KOH

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.05 – 7.88 (m, H-7, H-11, 2H), 7.67 – 7.62 (m, H-9, 1H), 7.58 – 7.53 (m, H-8, H-10, 2H), 5.78 – 5.65 (m, H-2, 1H), 5.15 – 5.09 (d, H-1, 2H), 3.85 (d, H-3, 2H), 3.79 (t, H-4, 2H), 3.41 (t, H-5, 2H) ppm.

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 140.1 (C-6), 133.8 (C-2, C-9), 129.3 (C-8, C-10), 128.2 (C-7, C-11), 117.7 (C-1), 72.2 (C-3), 63.5 (C-4), 56.5 (C-5) ppm.

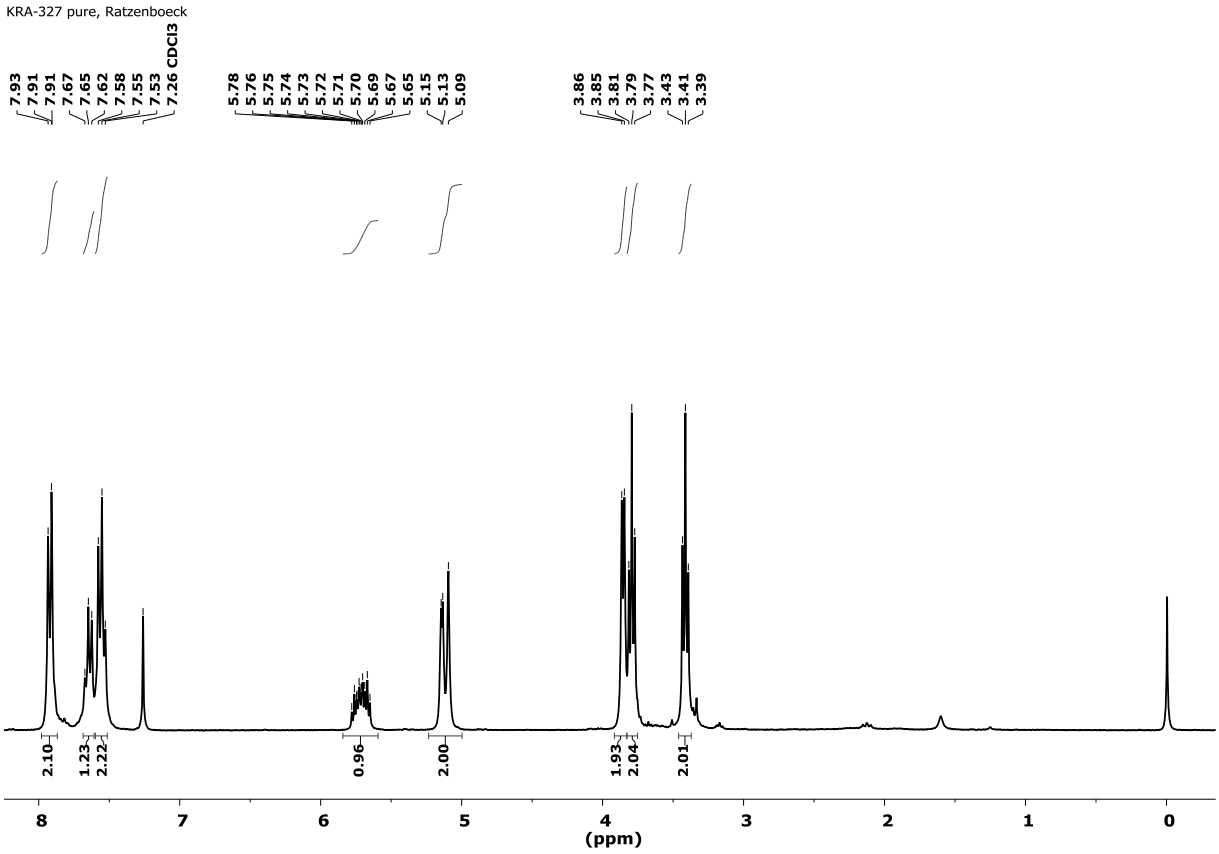


Figure S11. ^{1}H-NMR spectrum of **8** in $CDCl_3$.

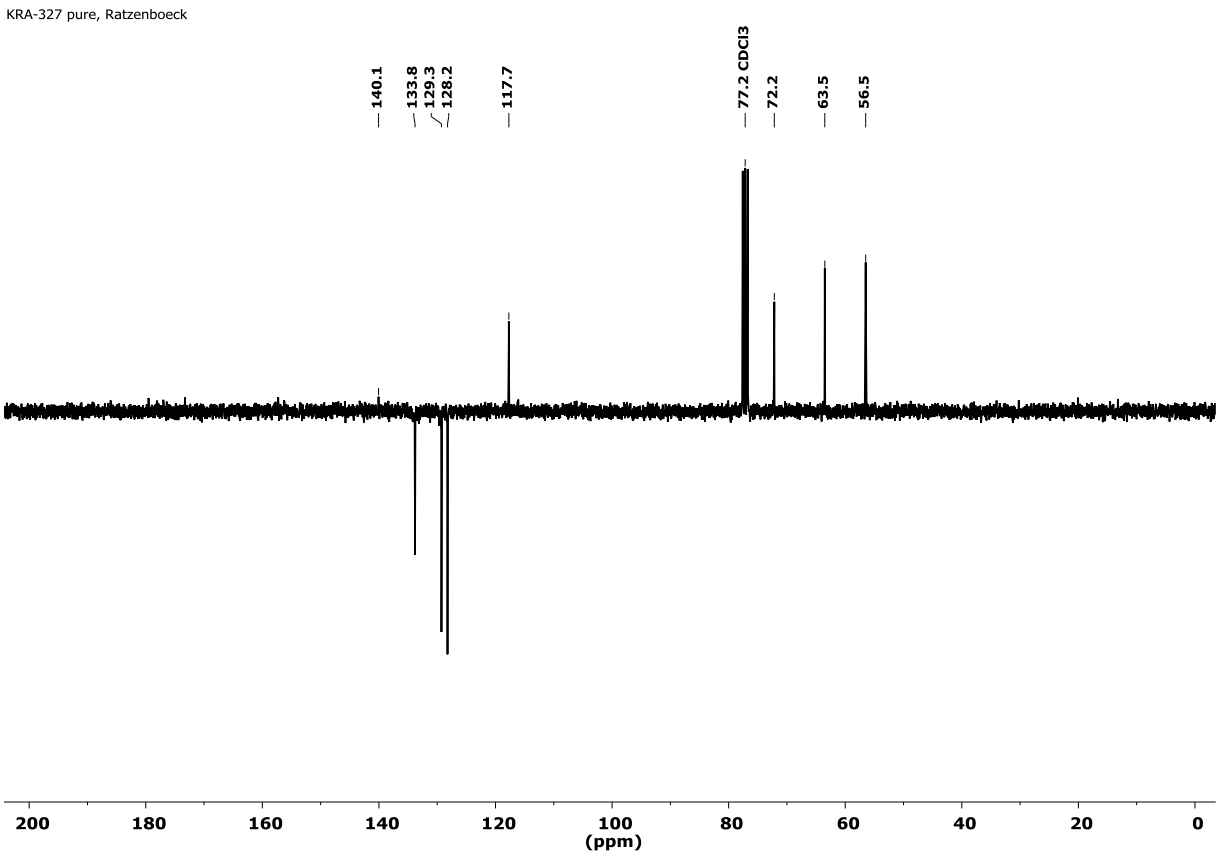


Figure S12. ^{13}C/APT-NMR spectrum of **8** in $CDCl_3$.

3. Retro oxa-Michael screenings

General procedure for catalyst screening in retro-Michael reaction:

In a sealed 4 mL reaction vessel 96.4 mg (0.450 mmol, 1.0 equiv.) ((2-(methylsulfonyl)ethoxy)methyl)benzene (**1**), 78.4 mg (1.35 mmol, 3.0 equiv.) allyl alcohol and 10 mol% of the respective catalyst were mixed together. The mixture was heated to 140 °C and full solubility of the catalyst was noted in all cases. After 1 h and 24 h reaction time an aliquot of the reaction mixture was analyzed by ^{1}H-NMR spectroscopy.

General procedure for temperature screening in retro-Michael reaction:

In a sealed 4 mL reaction vessel 96.4 mg (0.450 mmol, 1.0 equiv.) ((2-(methylsulfonyl)ethoxy)methyl)benzene (**1**), 78.4 mg (1.35 mmol, 3.0 equiv.) allyl alcohol and 10 mol% DBU or 5 mol% KOH were mixed together. The mixture was heated to the respective temperature (80 °C, 120 °C, 140 °C, 180 °C). After 15 min, 1 h and 24 h reaction time an aliquot of the reaction mixture was analyzed by ^{1}H-NMR spectroscopy.

General procedure for alcohol screening in retro-Michael reaction:

In a sealed 4 mL reaction vessel, 1.0 equiv. (0.40 mmol) oxa-Michael adduct **1-5**, 3.0 equiv. (1.2 mmol) allyl alcohol, benzyl alcohol, butanol, cyclopentanol or isobutanol and 5 mol% KOH were mixed together. The mixture was heated to the 140 °C. After 15 min, 1 h and 24 h reaction time an aliquot of the reaction mixture was analyzed by ^{1}H-NMR spectroscopy.

Monitoring of retro oxa-Michael by ^{1}H-NMR spectroscopy:

*Calculation of conversion of educt **1** to product **2**:*

$$product\ \mathbf{2}\ [\%] = \frac{\int C\boldsymbol{H}_2(allyl)(4.03\ ppm)}{\int C\boldsymbol{H}_2(benzyl)(4.56\ ppm) + \int C\boldsymbol{H}_2(allyl)(4.03\ ppm)} * 100$$

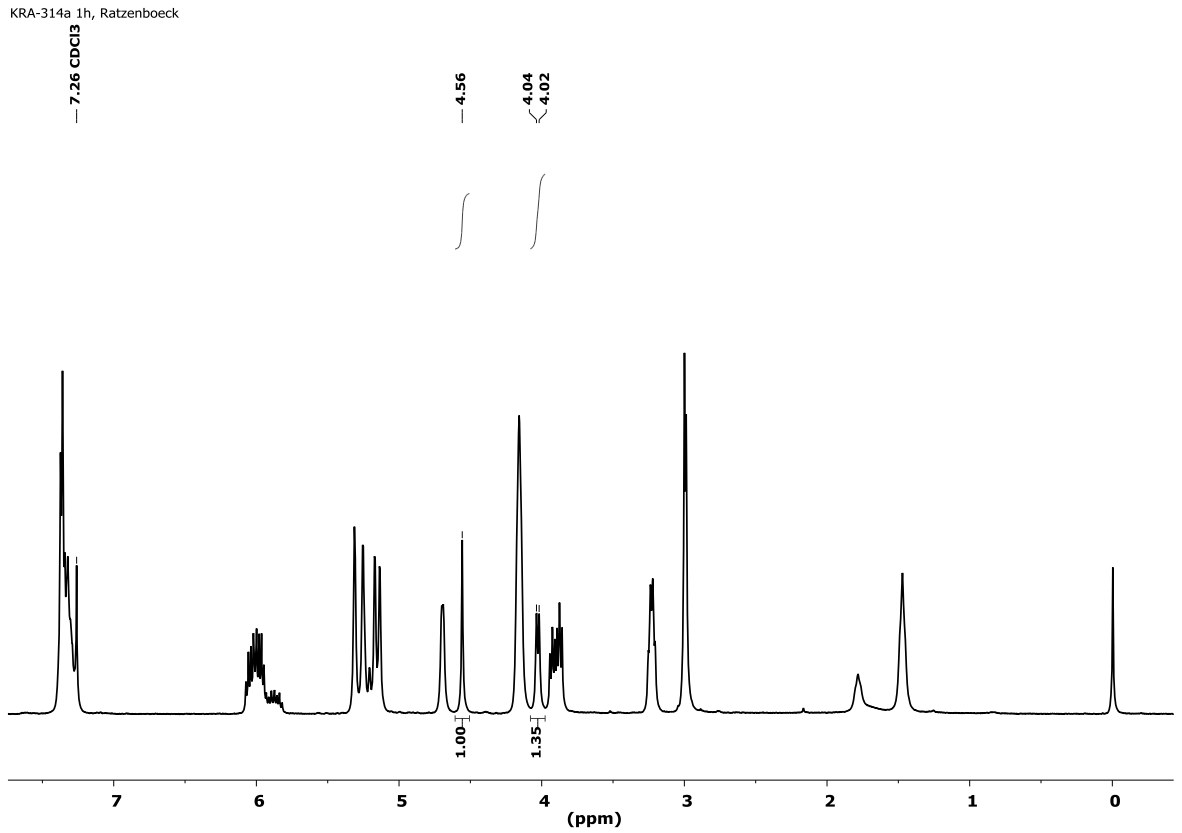


Figure S13: Exemplary ^{1}H-NMR spectrum of experiment presented in Figure 1b using 10 mol% KOH (140 °C) after 1 h reaction time in $CDCl_3$ with an educt : product ratio of 42.6% : 57.4%.

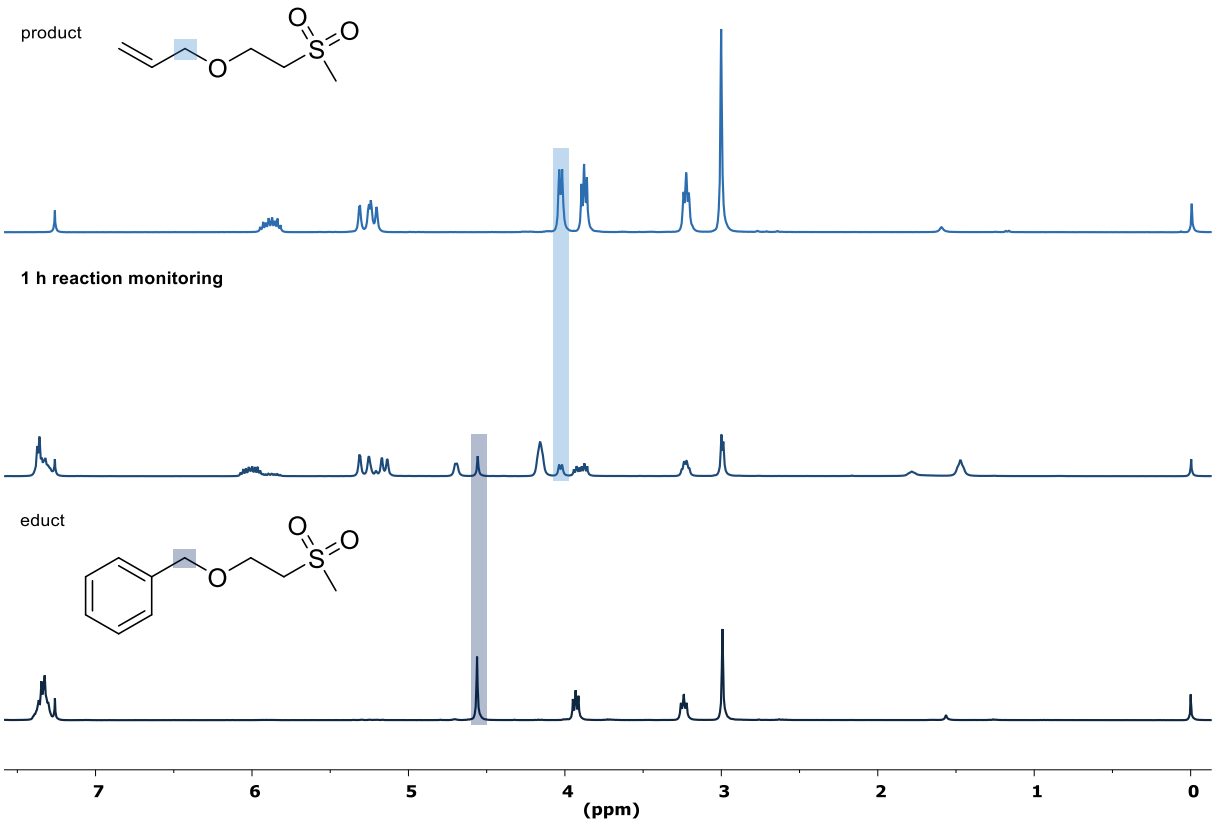


Figure S14: ^{1}H-NMR spectrum of experiment presented in Figure 1b (middle) compared with compounds **1** (bottom) and **2** (top).

For the calculation of the educt to product ratio in the alcohol screening, NMR shifts presented in Table S1 were selected.

Table S1: Selected ^{1}H-NMR shifts of respective oxa-Michael adducts to calculate educt to product ratio (integrals of noted peaks are equivalent to a CH_2 group, in case of CH the integral is multiplied by two)

educt : product - NMR shifts [ppm]					
	allyl alcohol	**benzyl alcohol**	**butanol**	**isobutanol**	**cyclopentanol**
cyclpentanol – MVS adduct **3**	3.80 : 4.03	3.80 : 4.56	(3.80-3.47) : 3.47	3.80 : (3.80 - 2*3.93)	-
isobutanol – MVS adduct **4**	(3.84-4.03) : 4.03	3.84 : 3.93	(3.84-3.47) : 3.47	-	(3.84-3.94) : (2*3.94)
butanol – MVS adduct **5**	3.47 : 4.03	3.47 : 4.56	-	3.47 : (3.84-3.47)	3.47 : (3.80-3.47)
benzyl alcohol – MVS adduct **1**	4.56 : 4.03	-	4.56 : 3.47	4.56 : 3.84	4.56 : 3.80
allyl alcohol – MVS adduct **2**	-	4.03 : 4.56	4.03 : 3.47	4.03 : (3.84-4.03)	4.03 : 3.80

Screening of catalyst loading regarding KOH and DBU:

Table S2: Conversion of educt **1** to product **2** within 1 h and 24 h with various catalyst loading of KOH and DBU at 140 °C.

catalyst	**[mol%]**	**ratio 1 h [%]**		**ratio 24 h [%]**	
		educt **1**	product **2**	educt **1**	product **2**
KOH	10	42.6	57.4	47.4	52.6
	5	34.6	65.4	41.5	58.5
	2	61.3	38.7	61.7	38.3
DBU	10	43.9	56.1	41.3	58.7
	5	55.9	44.1	52.4	47.6

Reaction progress of retro Michael reaction:

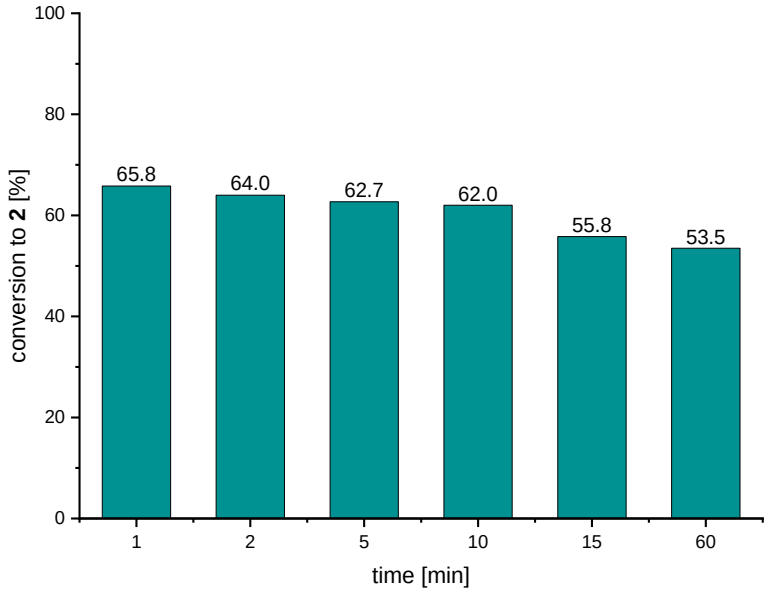


Figure S15: Monitoring reaction progress of educt **1** to product **2** at 140 °C with 5 mol% KOH over time.

Comparison of calculated and measured equilibrium constants:

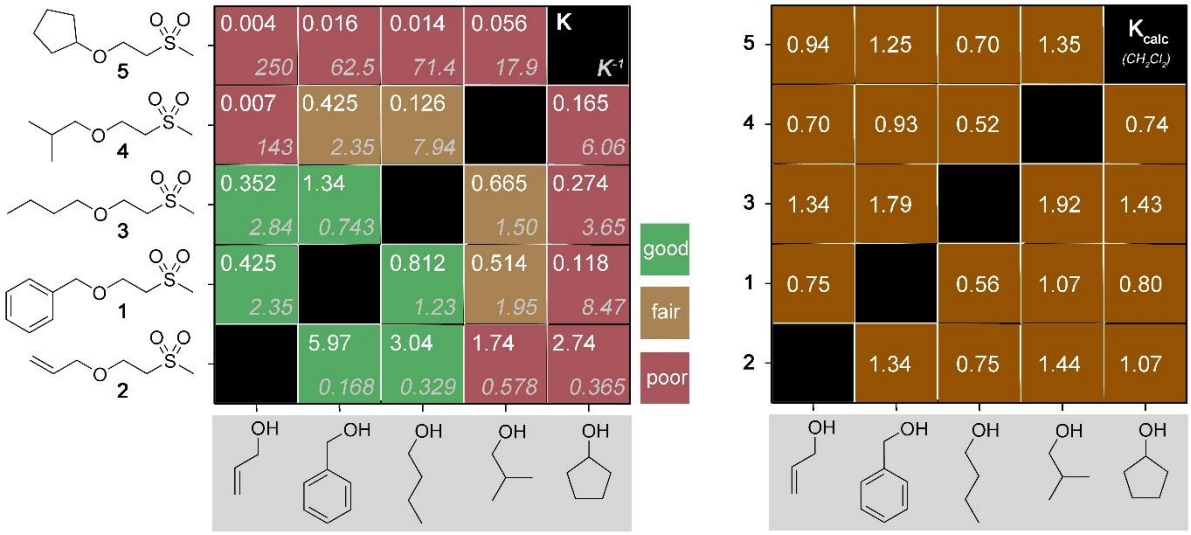


Figure S16: left) Experimental equilibrium constants; right) calculated equilibrium constants.

Computational Details

Conformational searches of all structures were performed with the COSMO-conf programme[2] at the PBE[3]-D3[4]/def2-SVPD level. The lowest energy structures were then reoptimized using PBE-D3/def2-SVPD as implemented in ORCA (version 5.0.2).[5] Confirmation of the minima, calculation of zero-point vibrational energies and thermal properties (at 25 °C) were performed by calculation of analytical normal modes using the rigid-rotor harmonic oscillator (RRHO) approximation. The structures were used as input geometries for further optimization using the double-hybrid functional B2-PLYP,[6] the def2-TZVPPD basis set and D3 dispersion correction. Solvent effects of dichloromethane have been approximated using the conductor-like polarizable continuum model (CPCM).[7] Our best estimate for calculation of Gibbs free energies (ΔG) resulted in using B2-PLYP-D3/def2-TZVPPD + Δsolv (B2-PLYP-D3) + ZPE, temp (PBE-D3/def2-SVPD).

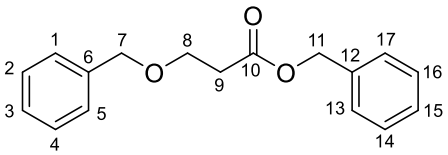
Gibbs free energies were obtained by calculating the energy differences between products and educts.

Equilibrium constants were determined using the Van't Hoff equation at 25 °C:

$$\Delta G = -RTln(K)$$

Study of acrylate based models:

Benzyl 3-(benzyloxy)propanoate (6)



In a 4 mL reaction vessel, 455 mg (4.21 mmol, 1.07 equiv.) benzyl alcohol, 641 mg (3.95 mmol, 1.00 equiv.) benzyl acrylate and 6.9 mol% (41 µL, 0.27 mmol) DBU were mixed together. The reaction was heated to 80 °C and stirred for 24 h. By ^{1}H-NMR spectroscopy a conversion of 90% was observed. The product was purified by flash column chromatography (silica gel, CH/EA 20:1 (v:v)). Isolated yield: 756 mg (70.8%)

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.35 – 7.26 (m, H-benzyl, 10H), 5.16 (s, H-11, 2H), 4.53 (s, H-7, 2H), 3.78 (t, H-8, 2H), 2.68 (t, H-9, 2H) ppm.

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 171.6 (C-10), 138.2 (C_q-benzyl), 136.1 (C_q-benzyl), 128.7 (C-benzyl), 128.5 (C-benzyl), 128.3 (C-benzyl), 127.8 (C-benzyl), 73.3 (C-7), 66.5 (C-11), 65.8 (C-8), 35.4 (C-9) ppm.

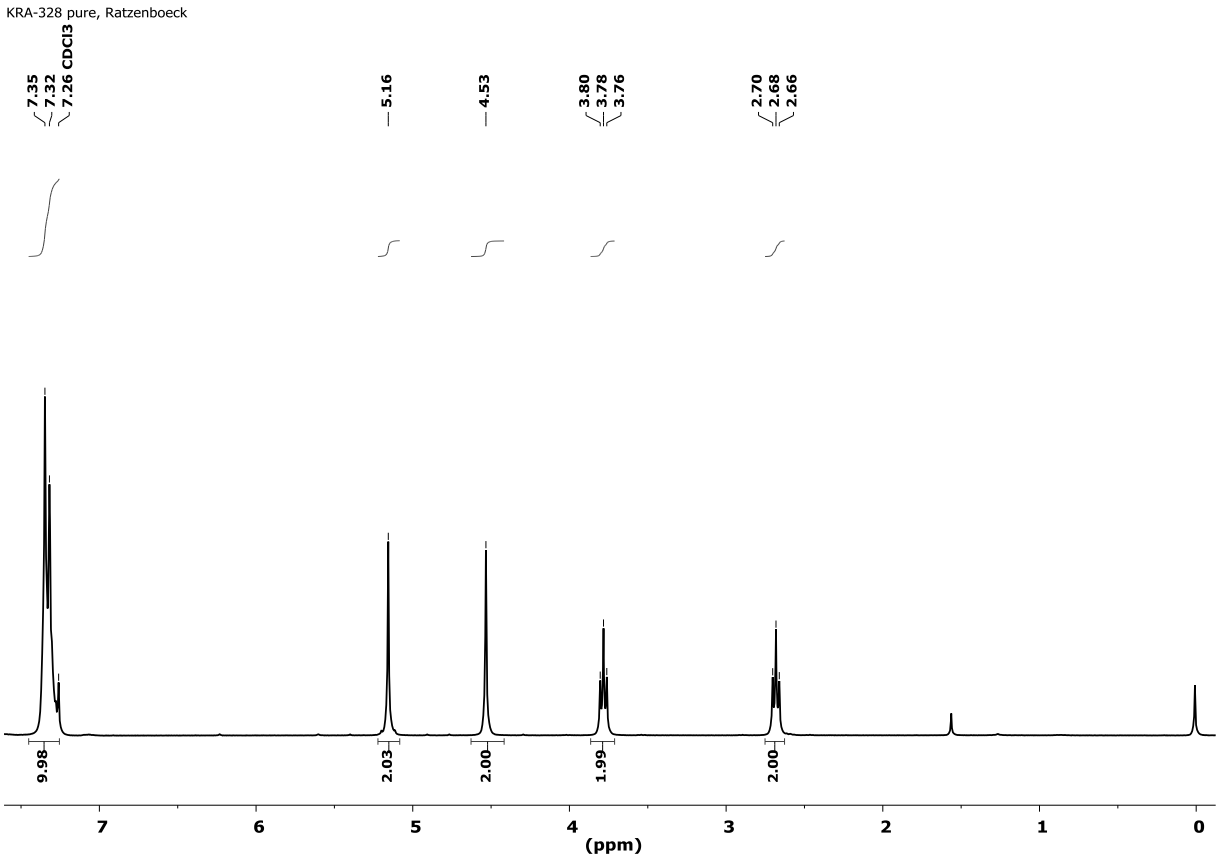


Figure S17. ^{1}H-NMR spectrum of **6** in $CDCl_3$.

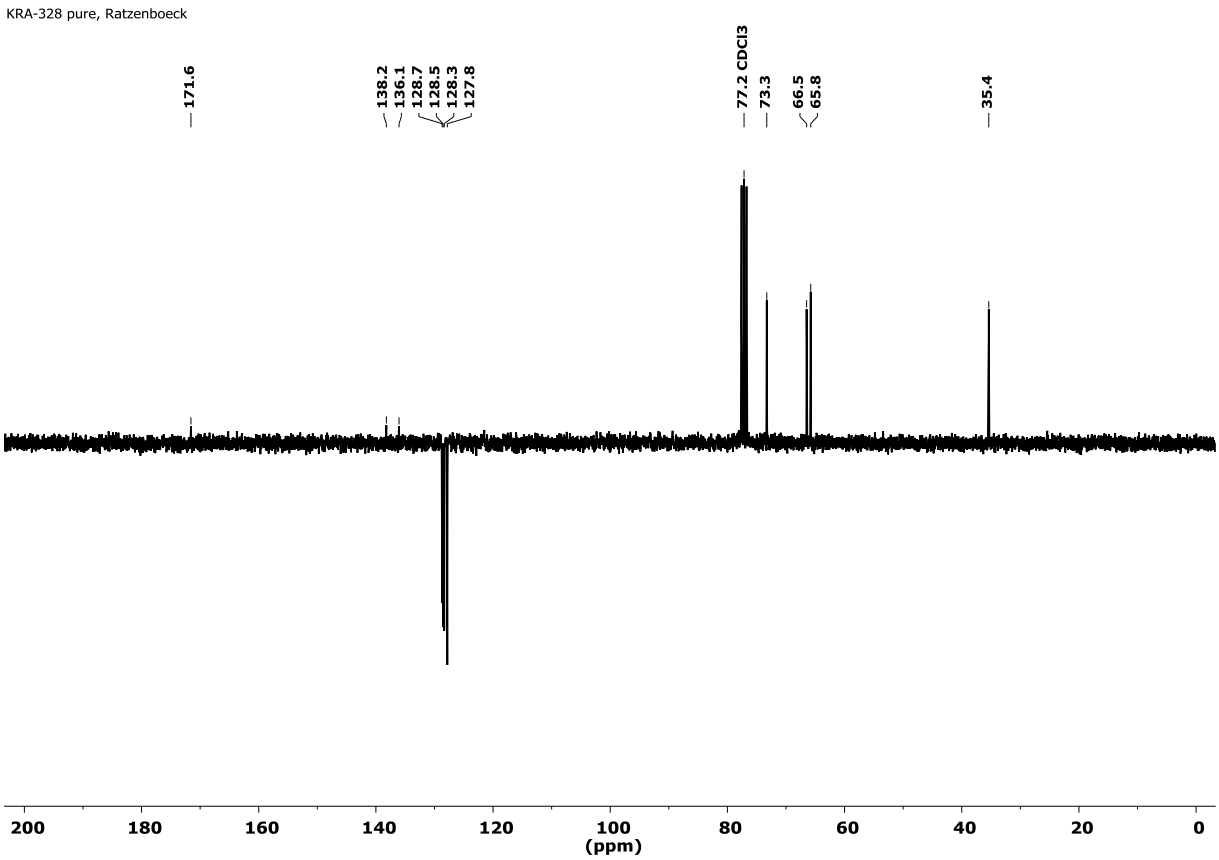


Figure S18. ^{13}C/APT-NMR spectrum of **6** in $CDCl_3$.

General procedure for demonstrating retro-Michael reaction of acrylate adducts:

In a sealed 4 mL reaction vessel 97.1 mg (0.359 mmol, 1.0 equiv.) benzyl 3-(benzyloxy)propanoate (**6**), 66.0 mg (1.14 mmol, 3.2 equiv.) allyl alcohol and 10 mol% of the respective catalyst (KOH or DBU) were mixed. The mixture was stirred at 140 °C. After 1 h and 24 h reaction time an aliquot of the reaction mixture was analyzed by ^{1}H-NMR spectroscopy.

Monitoring of retro oxa-Michael of acrylate adducts by ^{1}H-NMR spectroscopy:

Calculation of retro oxa-Michael:

$$allyl\ oxa-Michael\ product\ [\%] = \frac{\int \boldsymbol{CH}_2(allyl)(3.99\ ppm)}{\int \boldsymbol{CH}_2(benzyl+allyl)(3.78\ ppm)} * 100$$

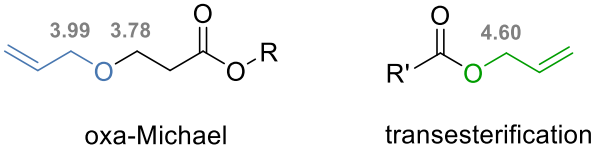
$$benzyl\ oxa-Michael\ educt\ [\%] = 100 - allyl\ oxa-Michael\ product$$

Calculation of transesterification:

$$allyl\ transesterificaton\ product\ [\%] = \frac{\int \boldsymbol{CH}_2(allyl\ ester)(4.60\ ppm)}{\int \boldsymbol{CH}_2(benzyl+allyl)(3.78\ ppm)} * 100$$

$$benzyl\ transesterificaton\ product\ [\%] = 100 - \ allyl\ transesterificaton\ product$$

In the calculation free vinyl groups (observed by ^{1}H-NMR spectroscopy) are not considered.



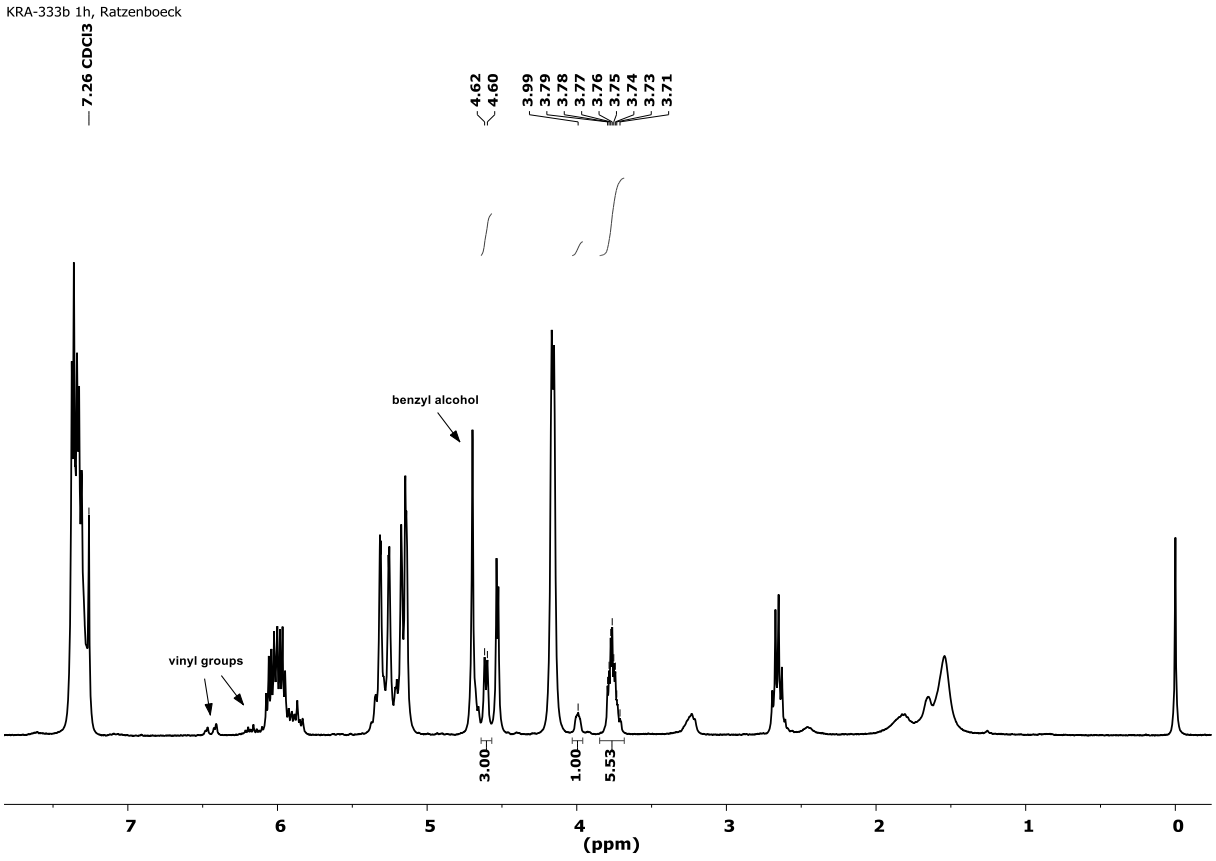


Figure S19: Exemplary ^{1}H-NMR spectrum of experiment presented in Figure 3 using 10 mol% DBU (140 °C) after 1 h reaction time in $CDCl_3$.

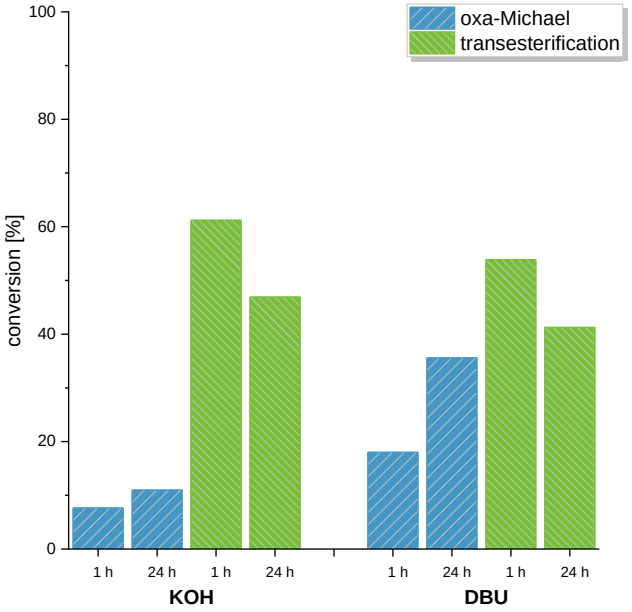
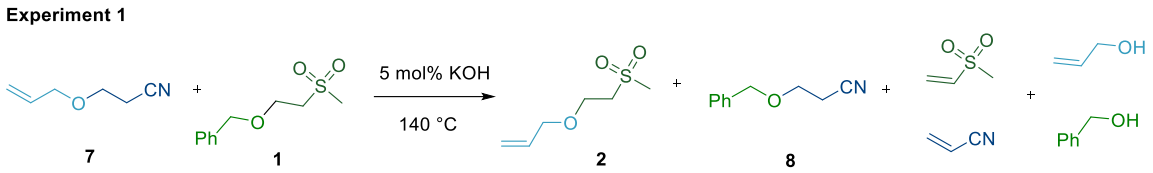
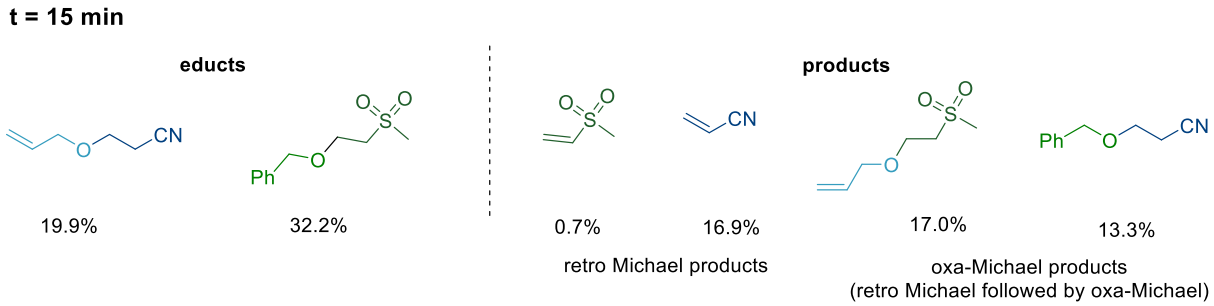


Figure S20: Retro oxa-Michael versus transesterification for acrylate-based model (Figure 3) monitored by ^{1}H-NMR spectroscopy over time (1 h, 24 h).

Scrambling of oxa-Michael adducts



	educts		products			
time [min]	**7**	**1**	**methyl vinyl sulfone**	**acrylonitril**	**2**	**8**
0	50.0	50.0	0.0	0.0	0.0	0.0
15	19.9	32.2	0.7	16.9	17.0	13.3



Scheme S1: Reaction of oxa-Michael adduct **1** with 3-(allyloxy)propanenitrile (**7**) at 140 °C with KOH and distribution of educts and products formed by retro Michael and oxa-Michael reaction.

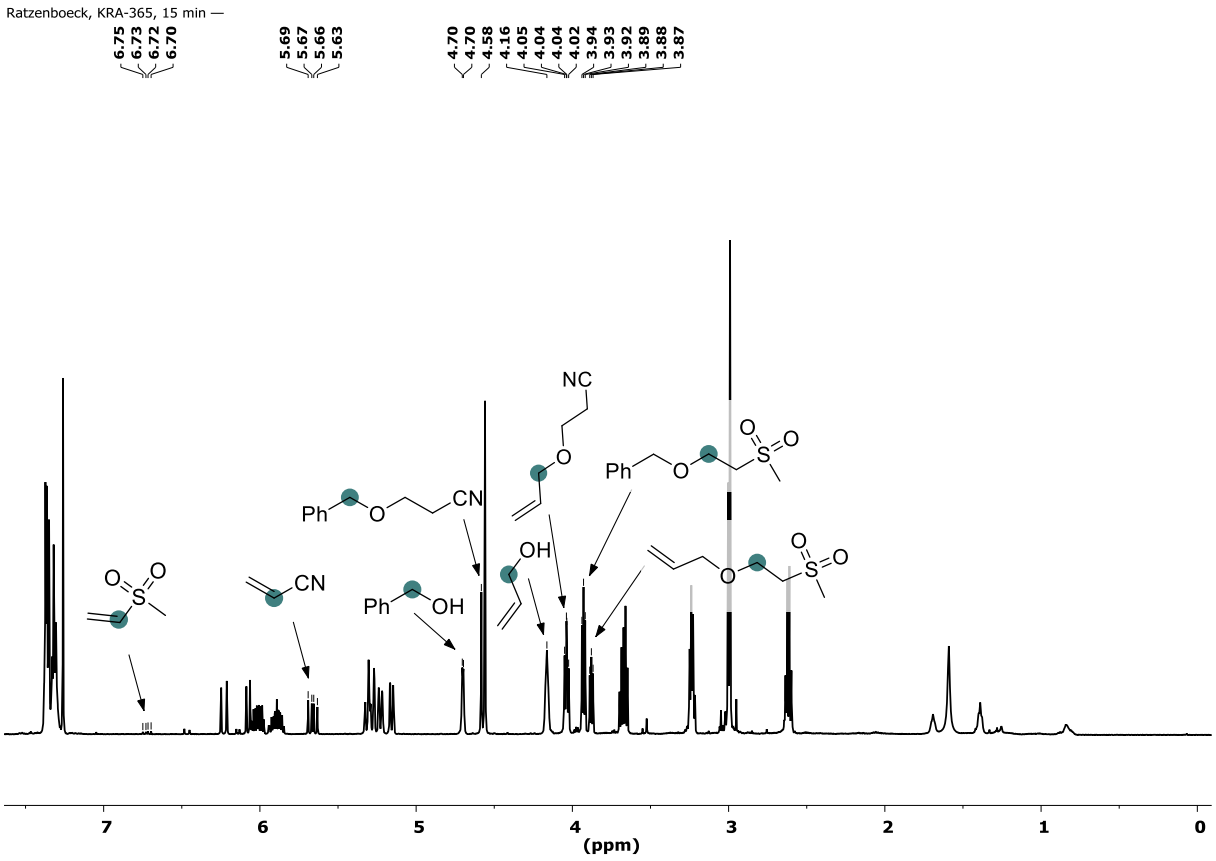
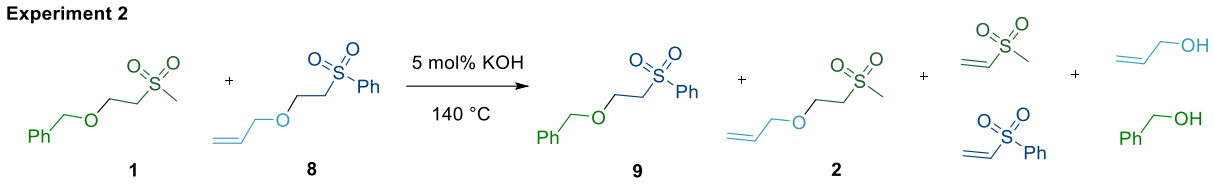


Figure S21: ^{1}H-NMR spectrum of scrambling of oxa-Michael adducts presented in Scheme S1 in $CDCl_3$.



	educts		products			
time [min]	**1**	**8**	**methyl vinyl sulfone**	**phenyl vinyl sulfone**	**9**	**2**
0	51.0	49.0	0.0	0.0	0.0	0.0
15	46.3	39.9	0.6	4.1	5.1	4.0

Scheme S2: Reaction of oxa-Michael adduct **1** with adduct of phenyl vinyl sulfone and allyl alcohol (**8**) at 140 °C with KOH and distribution of educts and products formed by retro Michael and oxa-Michael reaction.

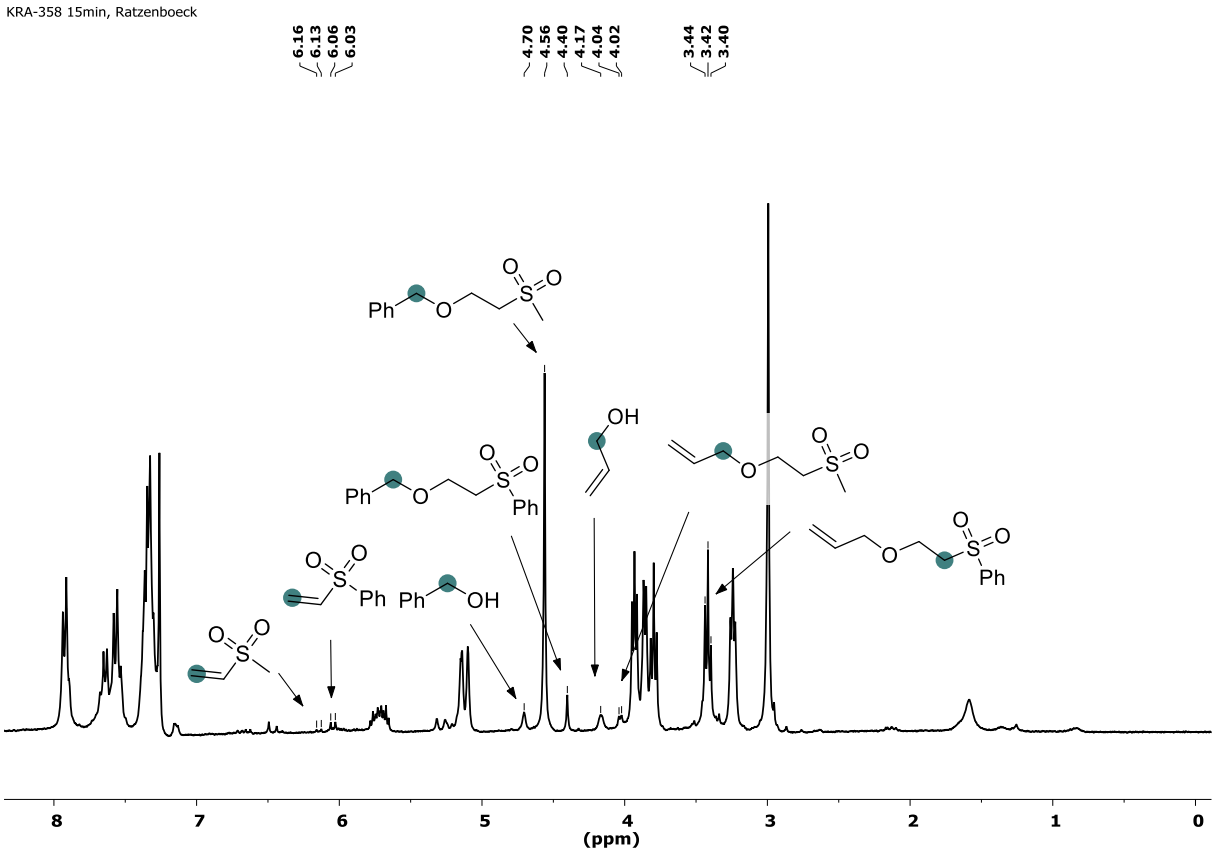
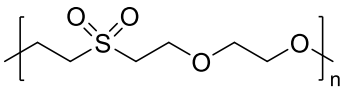


Figure S22: ^{1}H-NMR spectrum of scrambling of oxa-Michael adducts presented in Scheme S1 in $CDCl_3$.

4. Retro oxa-Michael in polymerization

General procedures for oxa-Michael polymerization:

Poly1 – polyaddition of ethylene glycol and divinyl sulfone**:**

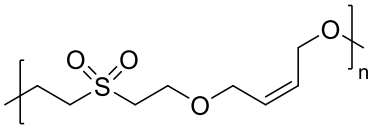


poly1

Poly1 was synthesized according to modified literature procedure.[8] In a sealed 4 mL reaction vessel 5.0 mol% of the respective catalyst (KOH, KO^{t}Bu, PPh_3, DMAP) was dissolved in 62.0 mg (1.00 mmol, 1.0 equiv.) ethylene glycol. Subsequently, 118 mg (1.00 mmol, 1.0 equiv.) divinyl sulfone was added at room temperature. The reaction mixture was stirred for 5 min at which point it turned highly viscous. After 24 h reaction time ^{1}H-NMR data is in accordance with literature.[8]

For purification, the polymer was taken up in methylene chloride (2 mL) and the organic layer was extracted with 1 M HCl (1 mL). The organic layer was washed with brine (3 x 2 mL), dried over Na_2SO_4 and filtered. The solvent was removed by vacuum yielding a yellow, highly viscous product.

Poly2 – polyaddition of (*Z*)-2-butene-1,4-diol and divinyl sulfone**:**



poly2

Poly2 was synthesized according to modified literature procedure.[8] In a sealed 4 mL reaction vessel 4.9 mol% (7.1 mg, 0.127 mmol) KOH was dissolved in 226 mg (2.56 mmol, 1.0 equiv.) (*Z*)-2-butene-1,4-diol. Subsequently, 304 mg (2.57 mmol, 1.0 equiv.) divinyl sulfone was added at room temperature. The reaction mixture instantly turns highly viscous. After 24 h reaction time ^{1}H-NMR data is in accordance with literature.[8] **Poly2** was further used without any work-up.

Properties of poly1:

Table S3: Degradation onset temperature ($T_{d\,95\%}$) of **poly1** including bases (KOH or KO^{t}Bu) or nucleophiles (PPh_3 or DMAP) or no catalyst determined by TGA; molar mass determined by SEC after [a] 1 month/[b] 24 h reaction time + quenching.

	Thermal degradation		**Molar mass**	
	mass loss [%]	T [°C]	M_n [g/mol]	Dispersity
poly1 - KOH	5	195	2200 [a]	2.0
poly1 - KO^{t}Bu	5	193	2100 [a]	2.1
poly1 - PPh_3	5	215	2980 [a]	1.8
poly1 - DMAP	5	232	3260 [a]	1.9
poly1 - no cat.	10	323	1750 [b]	1.7

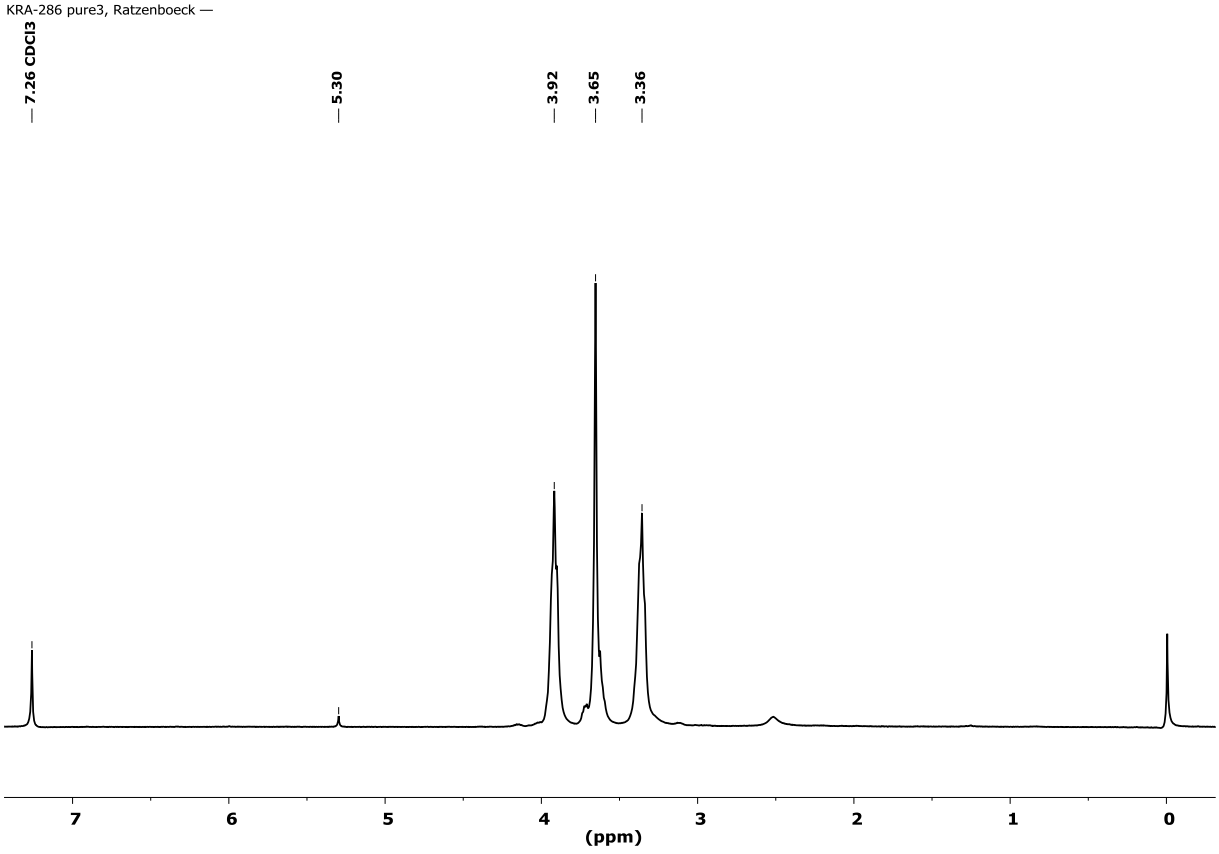


Figure S23: ^{1}H -NMR spectrum in $CDCl_3$ of **poly1** after drying in vacuum, still containing methylene chloride[9] from work up.

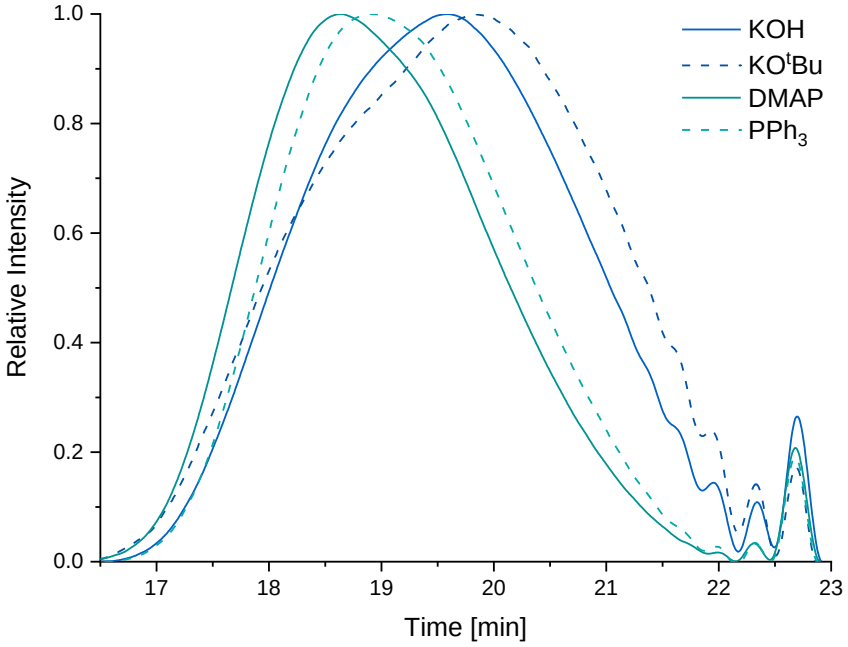
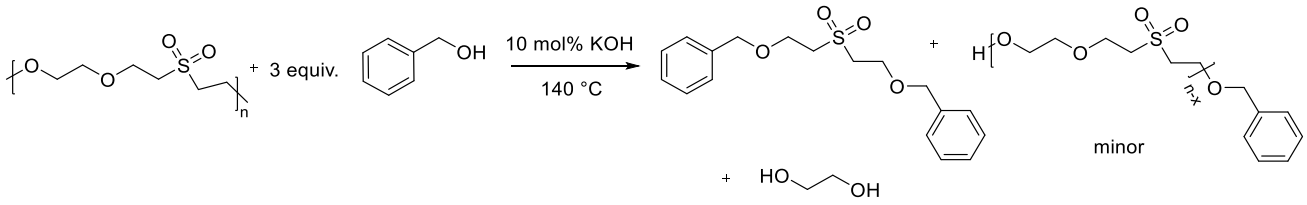


Figure S24: SEC of **poly1** including bases (KOH or KO^{t}Bu) or nucleophiles (PPh$_3$ or DMAP) after 1 month.

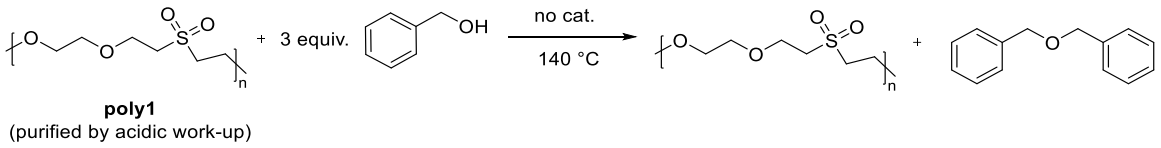
Depolymerization of poly1 with benzyl alcohol:

A sealed 4 mL reaction vessel was charged with 98 mg (0.54 mmol) **poly1**, 194 mg (1.79 mmol, 3.3 equiv.) benzyl alcohol and 4.9 mol% (1.5 mg, 0.027 mmol) KOH. The reaction mixture was stirred at 140 °C for 1 h (Scheme S3) whereupon a sample for ^{1}H-NMR spectroscopy was taken.



Scheme S3: Reaction of **poly1** and benzyl alcohol at 140 °C with KOH.

To demonstrate the necessity of a basic catalyst, the same procedure was repeated without any KOH (Scheme S4). Samples for NMR spectroscopy were taken after 1 h reaction time at 140 °C.



Scheme S4: Reaction of **poly1** and benzyl alcohol at 140 °C without any basic catalyst.

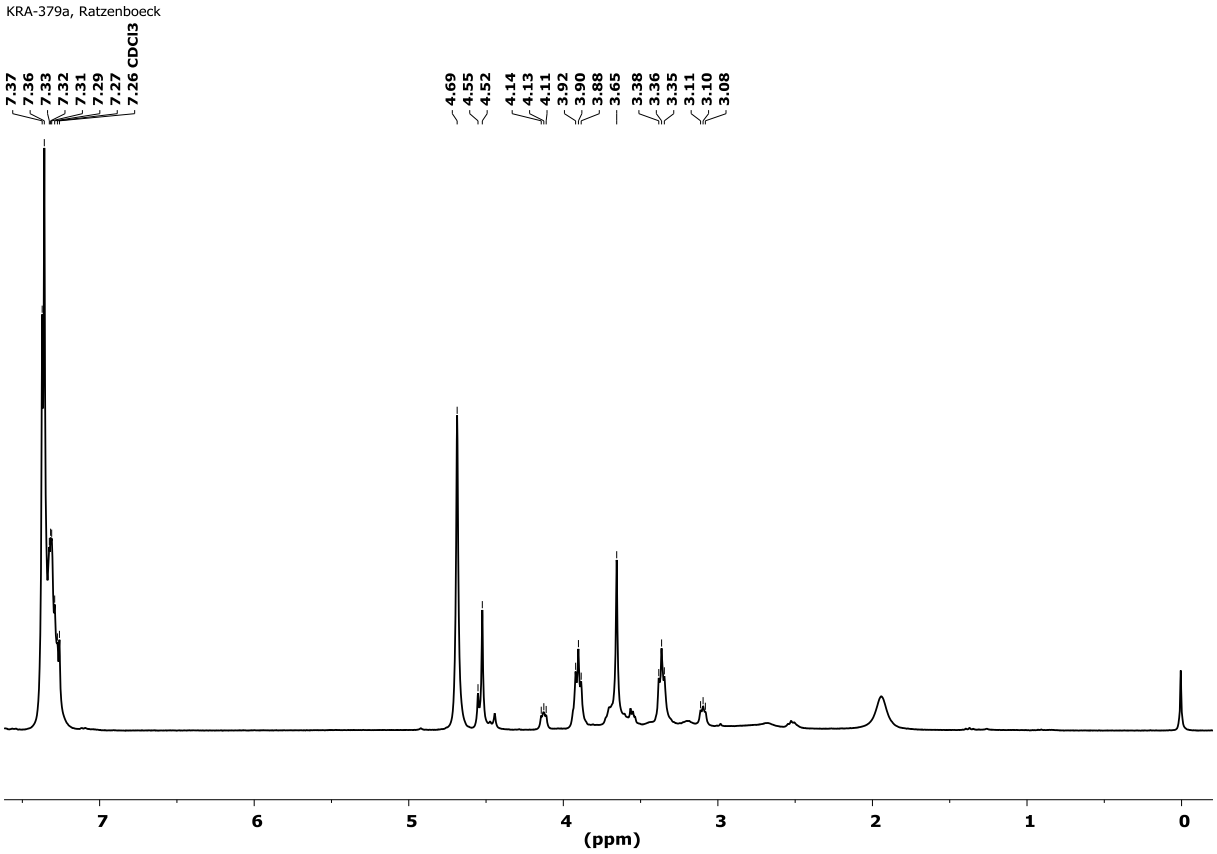


Figure S25. ^{1}H -NMR spectrum of reaction of **poly1** and benzyl alcohol at 140 °C with KOH as catalyst in $CDCl_3$.

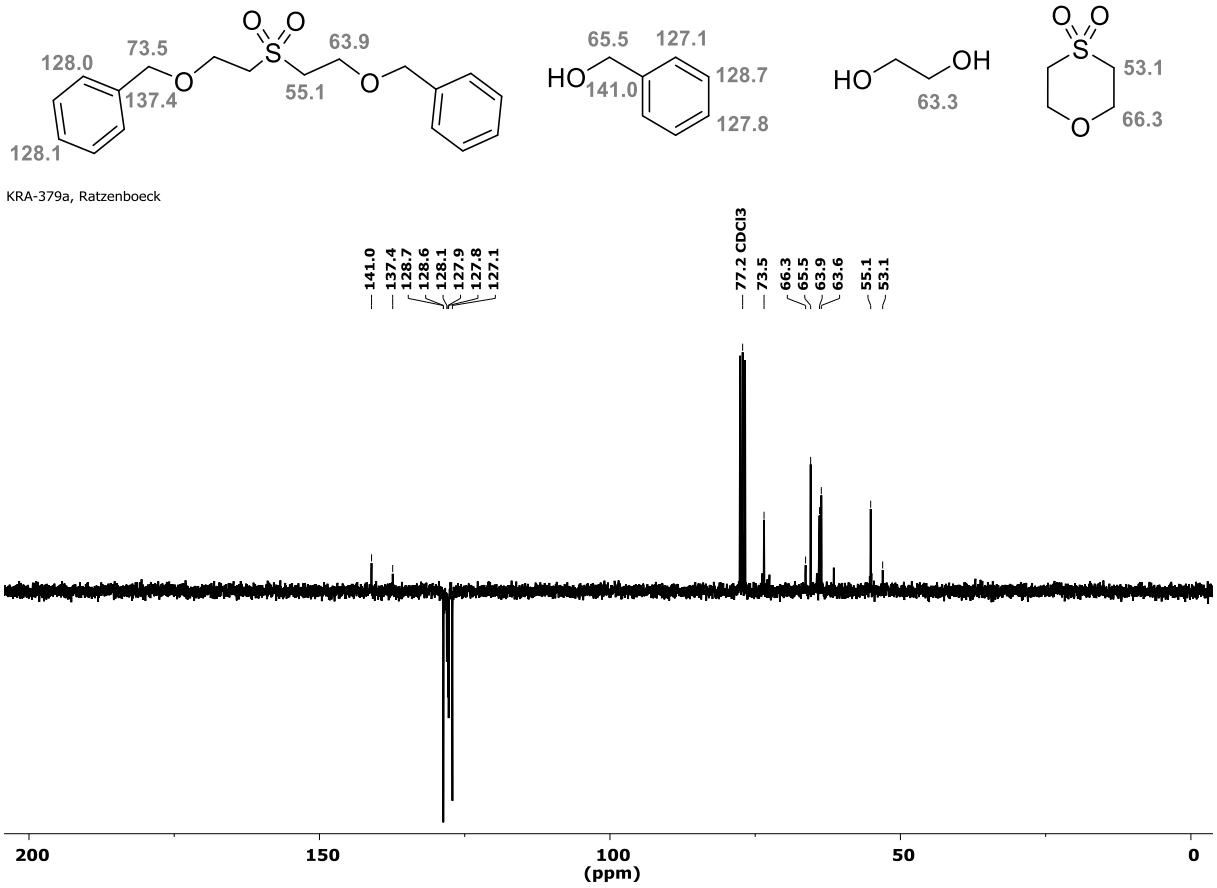


Figure S26. ^{13}C/APT-NMR spectrum of reaction of **poly1** and benzyl alcohol at 140 °C with KOH in $CDCl_3$.

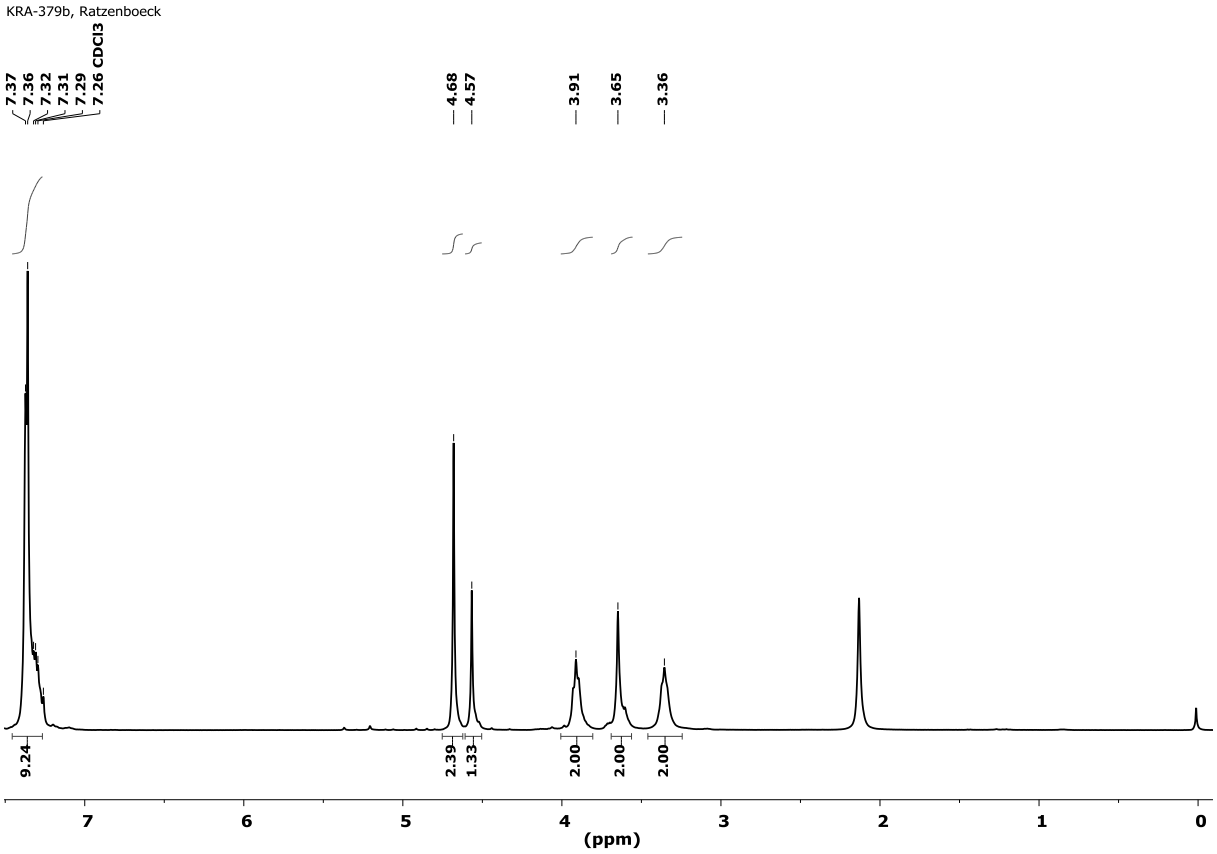


Figure S27. [1]H-NMR spectrum of reaction of **poly1** and benzyl alcohol at 140 °C without any catalyst in $CDCl_3$.

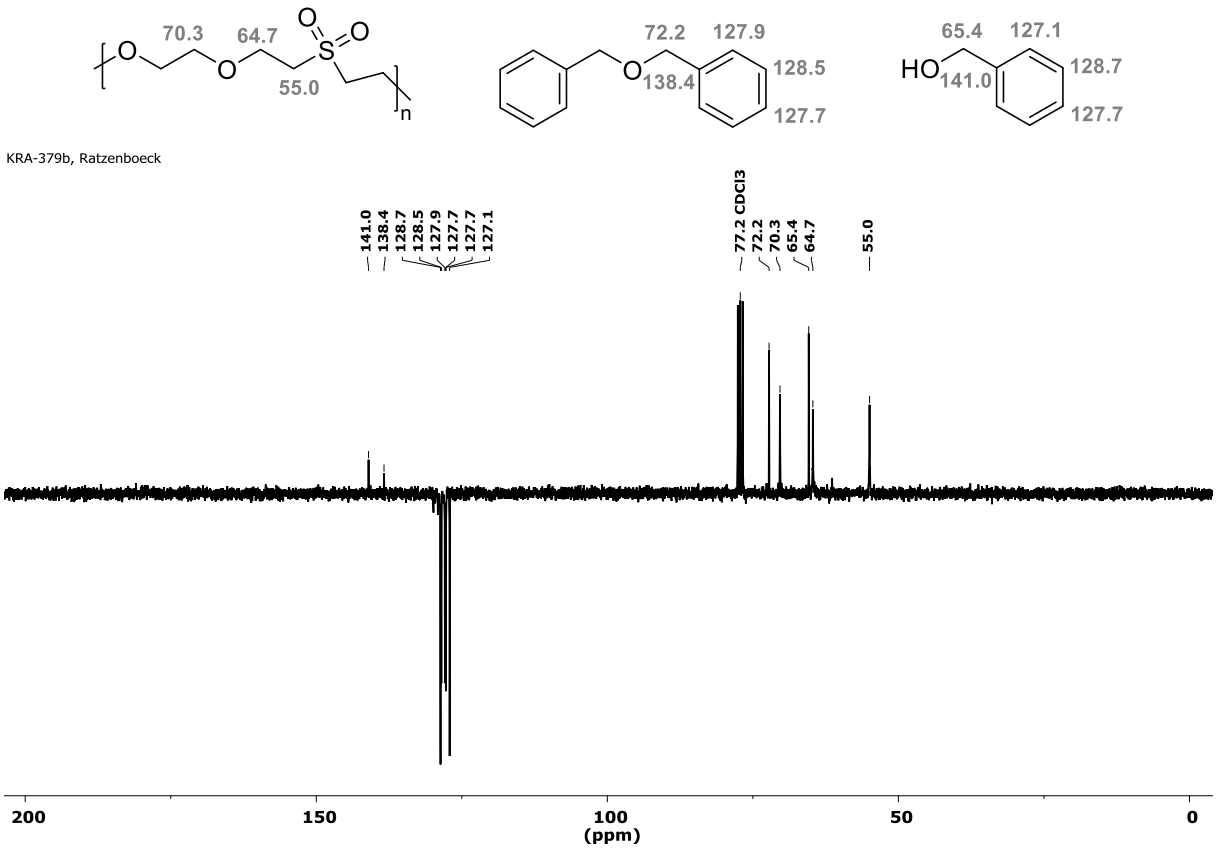


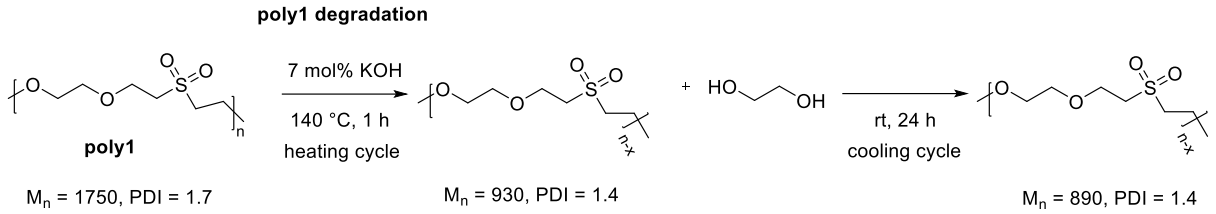
Figure S28. [13]C/APT-NMR spectrum of reaction of **poly1** and benzyl alcohol at 140 °C without any catalyst in $CDCl_3$.

Depolymerization of poly1:

In a sealed 4 mL reaction vessel 6.9 mol% (2.2 mg, 0.039 mmol) KOH was added to 101 mg (0.563 mmol) **poly1**-purified. The reagents were stirred at 140 °C for 1 h (heating cycle). Thereafter, the mixture was stirred 24 h at rt (cooling cycle).

Additionally, only **poly1**-purified (without any KOH) was heated to 140 °C and stirred for 1 h (heating cycle).

After the heating and cooling cycle, samples for SEC were taken and quenched with conc. acetic acid.



Scheme S5: Degradation of **poly1** by base catalysis at 140 °C (heating cycle) followed by stirring at rt.

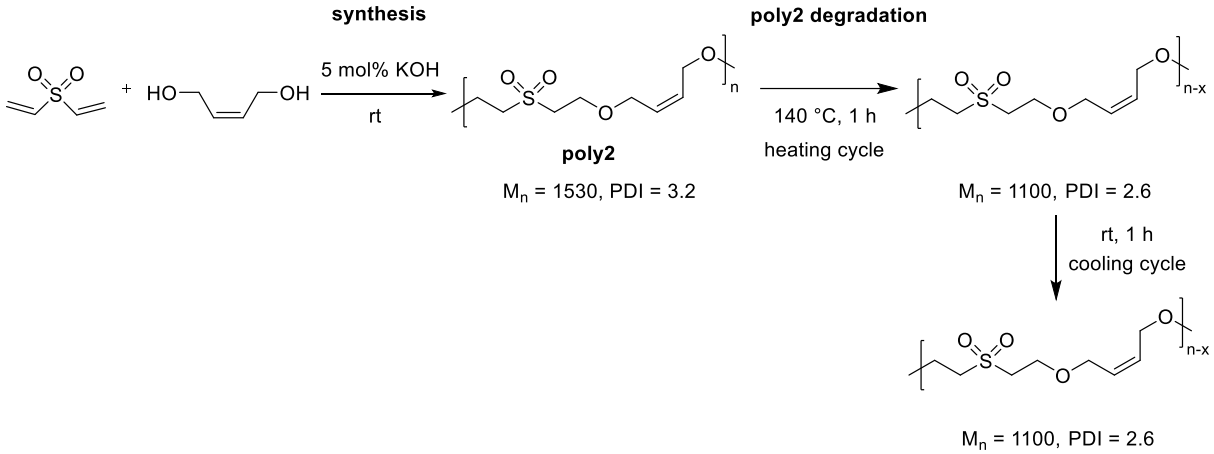
Table S4: SEC data of **poly1** and its depolymerization.

Sample	M_n [g/mol]	M_w [g/mol]	Dispersity
poly1	1750	3050	1.7
no cat., heating cycle	1810	2830	1.6
KOH, heating cycle	930	1260	1.4
KOH, cooling cycle (24 h)	890	1240	1.4

Depolymerization of poly2:

Poly2 was used as prepared. It was stirred in a sealed 4 mL reaction vessel at 140 °C for 1 h (heating cycle 1). Then the mixture was cooled to room temperature and further stirred for 1 h (cooling cycle 1). In the following the mixture was again heated to 140 °C for 1 h (heating cycle 2), followed by stirring at room temperature for 1 h (cooling cycle 2). This procedure was repeated a third time (heating / cooling cycle 3) and cooling cycle 3 was further extended to 24 h.

After each heating and cooling cycle a sample was taken for SEC and MALDI-TOF analysis and quenched with conc. acetic acid.



Scheme S6: Synthesis of **poly2** followed by the degradation of **poly2** (incl. basic catalyst) at 140 °C.

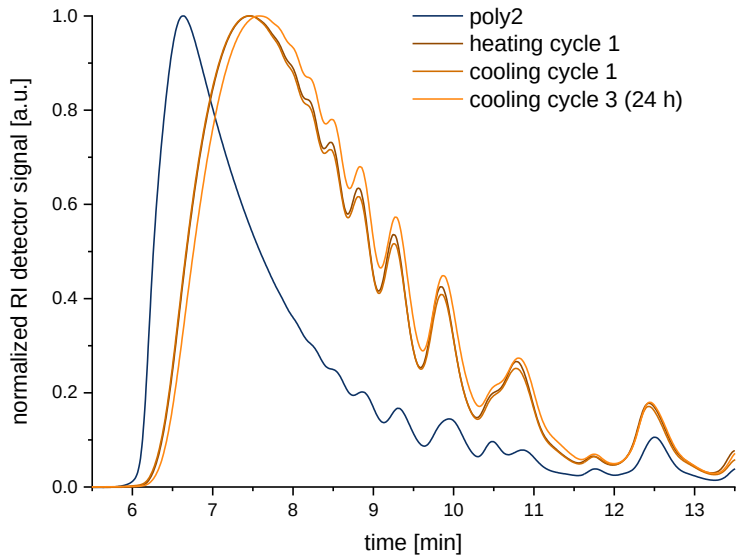


Figure S29: SEC of **poly2** before and after respective heating (140 °C for 1 h) and cooling (room temperature for 1 h or 24 h).

Table S5: SEC data of **poly2** and its depolymerization.

Sample	M_n [g/mol]	M_w [g/mol]	Dispersity
poly2	1530	4960	3.2
heating cycle 1	1100	2800	2.6
cooling cycle 1	1100	2800	2.6
heating cycle 2	1090	2670	2.5
cooling cycle 2	1080	2670	2.5
heating cycle 3	1060	2600	2.5
cooling cycle 3	1040	2550	2.5
cooling cycle 3 (24 h)	1060	2600	2.5

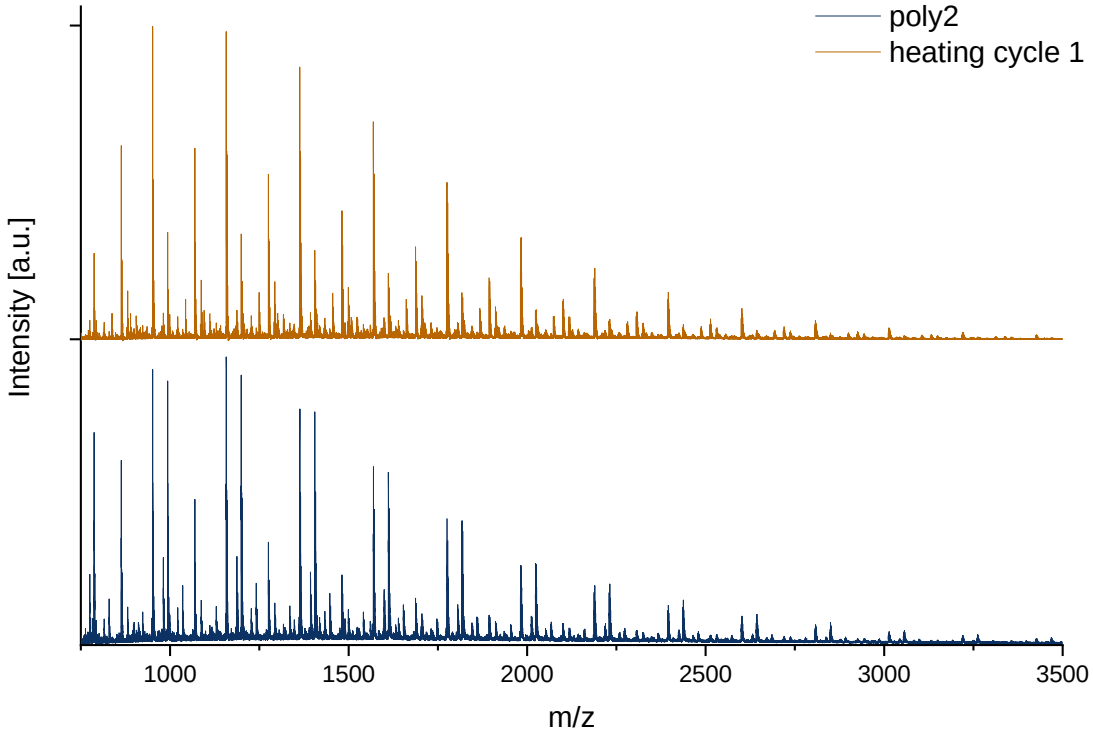


Figure S30: MALDI-TOF MS of **poly2** before and after respective heating (140 °C for 1 h).

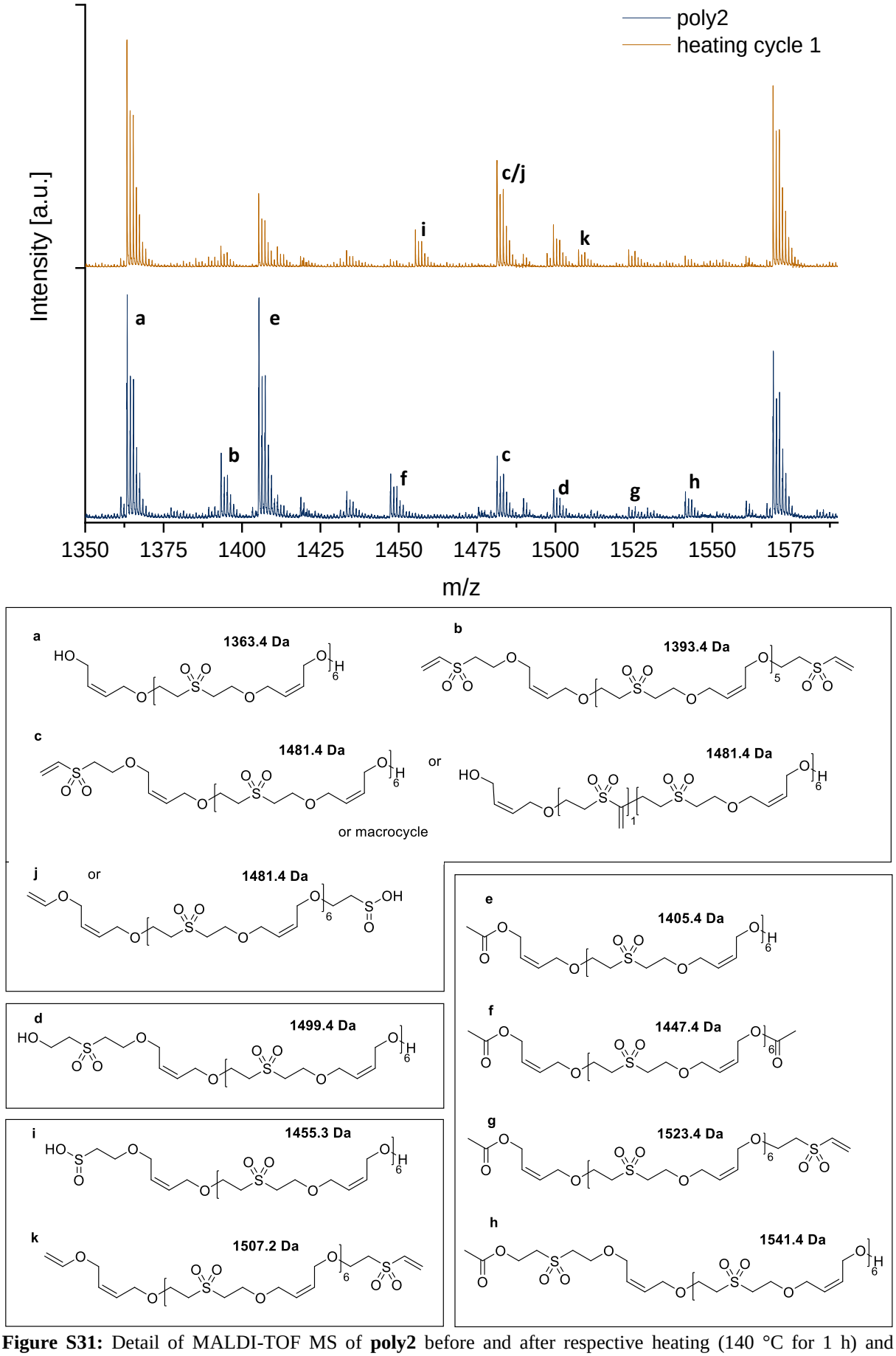


Figure S31: Detail of MALDI-TOF MS of **poly2** before and after respective heating (140 °C for 1 h) and assignment of detected species – calculated masses contain a potassium cation.

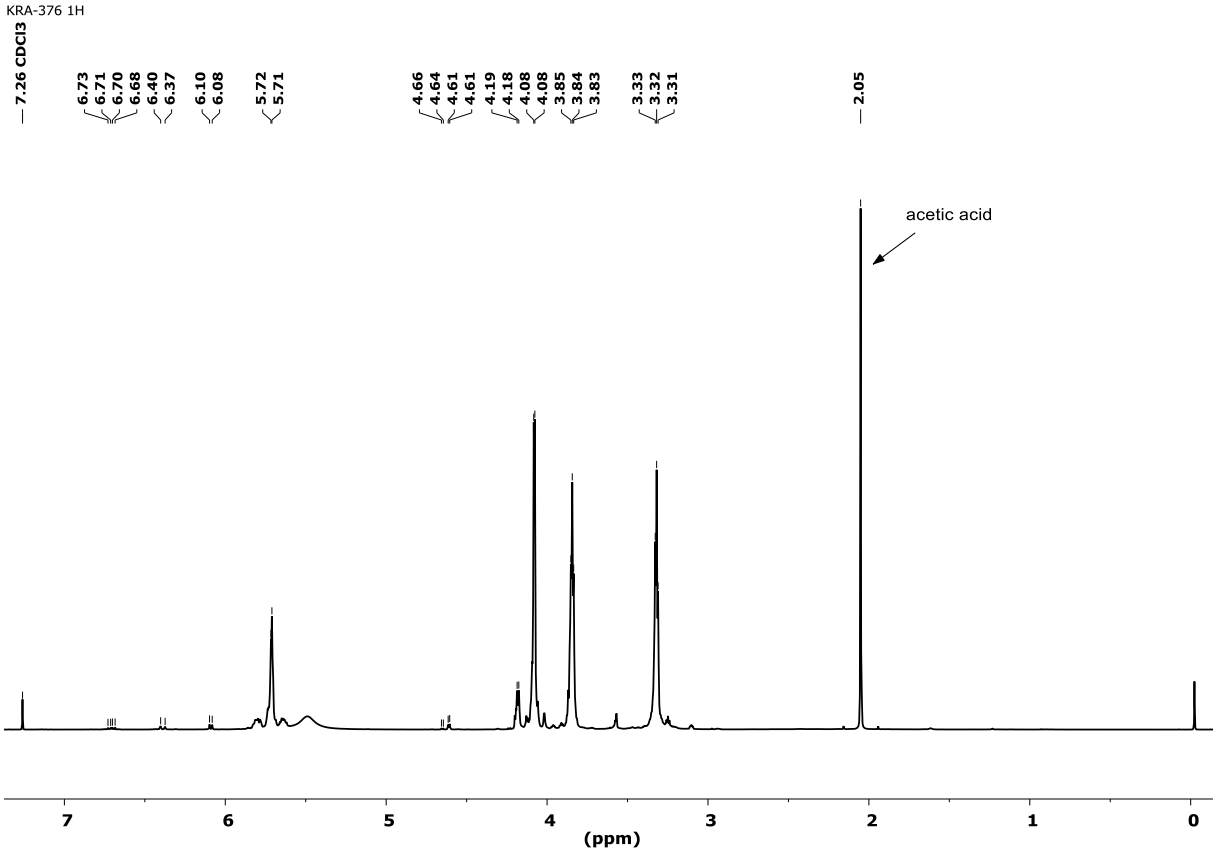
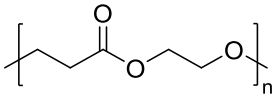


Figure S32. ^{1}H-NMR spectrum of **poly2** (heating cycle 1) in $CDCl_3$ quenched with acetic acid – acetate formation after 3 weeks.

Poly3 – oxa-Michael polymerization of 2-hydroxyethyl acrylate:



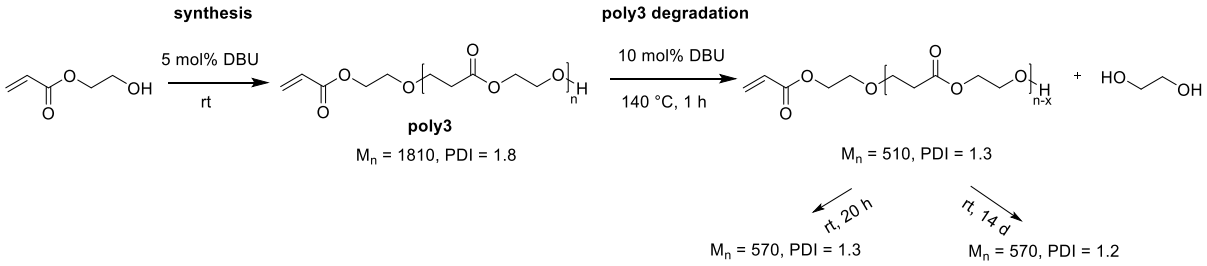
poly3

A sealed 4 mL reaction vessel was charged with 589 mg (5.1 mmol) 2-hydroxyethyl acrylate and 4.6 mol% (36 mg, 0.236 mmol) 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). The reaction mixture was stirred for 24 h at room temperature. **Poly3** was further used without any work-up.

^{1}H-NMR data is in accordance with literature.[1]

Depolymerization of poly3:

A sealed 4 mL reaction vessel was charged with 112 mg (0.956 mmol) **poly3** (sample 21 d) and 9.8 mol% (14.2 mg, 0.093 mmol) DBU. The reaction mixture was stirred at 140 °C for 1 h (heating cycle). A sample was taken for SEC analysis and quenched with 1 M HCl. The mixture was further stirred at room temperature. After 20 h and 2 weeks another sample was taken for SEC analysis (cooling cycle).



Scheme S7: Homopolymerization of HEA giving **poly3** followed by the degradation of **poly3** upon treatment with base and temperature.

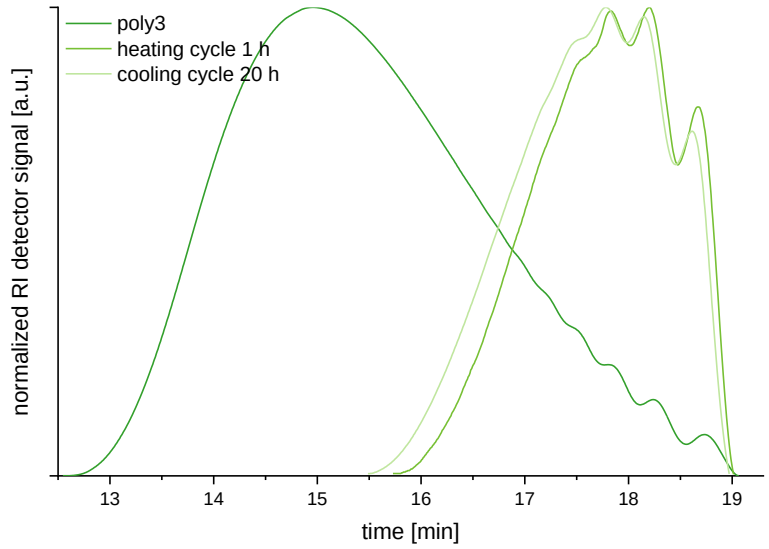


Figure S33: SEC of **poly3** before and after the treatment with DBU at 140 °C for 1 h (heating cycle), and after the cooling cycle (20 h at room temperature).

Table S6: SEC data of **poly3** and its depolymerization.

Sample	Time	M_n [g/mol]	M_w [g/mol]	Dispersity
poly3	1 d	1060	1700	1.6
poly3	21 d	1810	3350	1.8
poly3 (heating cycle)	1 h	510	670	1.3
poly3 (cooling cycle)	20 h	570	750	1.3
poly3 (cooling cycle)	14 d	570	700	1.2

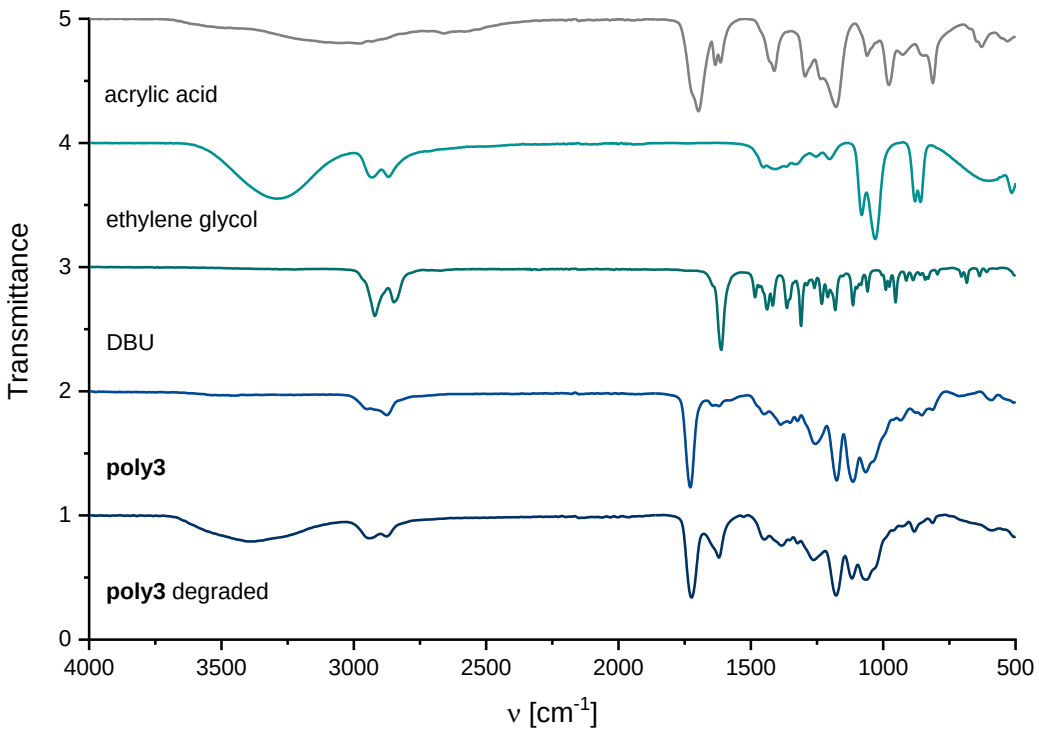


Figure S34: IR specta of **poly3** before (2) and after (1) the treatment with DBU at 140 °C for 1 h (heating cycle) and reference spectra for acrylic acid (5), ethylene glycol (4) and DBU (3).

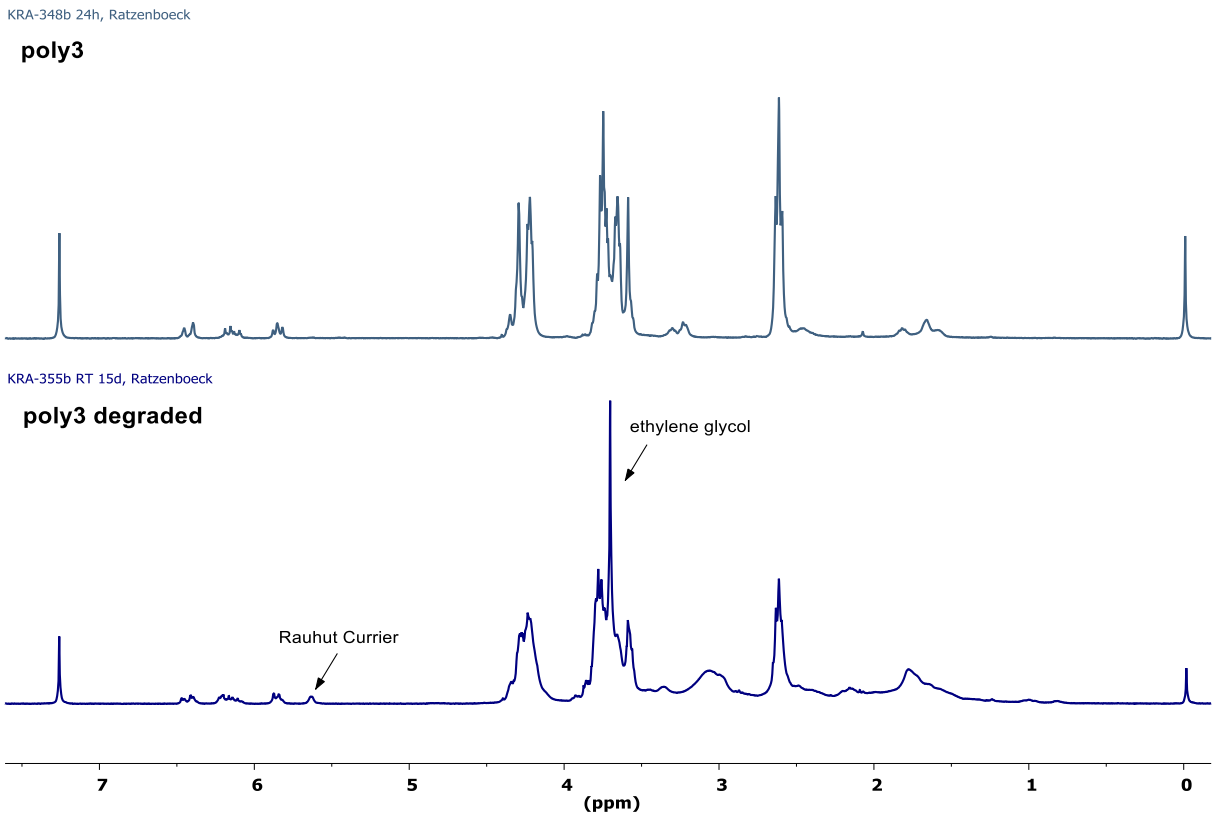


Figure S35. ^{1}H-NMR spectrum of **poly3** (top) versus **poly3 degraded** (bottom) in $CDCl_3$.

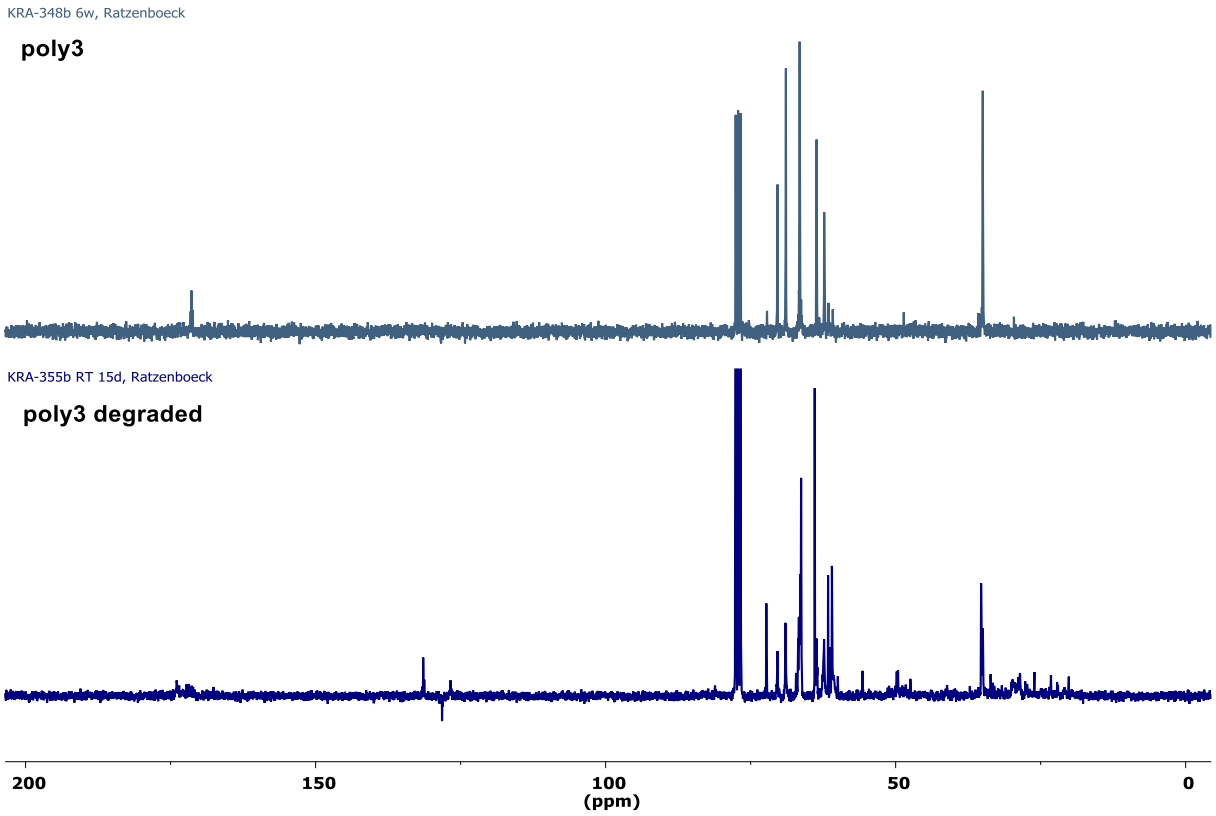
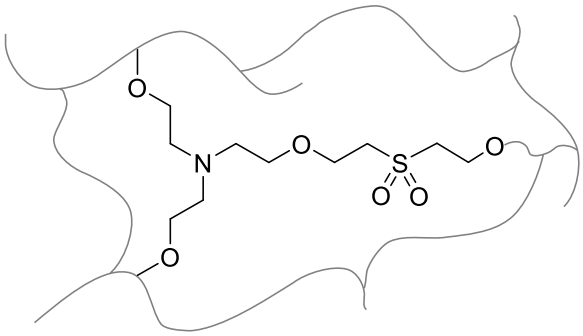


Figure S36. ^{13}C/APT-NMR spectrum of **poly3** (top) versus **poly3 degraded** (bottom) in $CDCl_3$.

5. Self-healing of oxa-Michael networks

Poly4 – oxa-Michael polymer network of divinyl sulfone and triethanolamine:



A 20 mL reaction vessel was charged with 2.36 g (20 mmol, 1.0 equiv.) divinyl sulfone and half of the necessary amount of triethanolamine (1.99 g (13.3 mmol, 1.0 equiv.)). The other half of triethanolamine was mixed with 10 mol% (304 mg, 2.0 mmol) DBU. The alcohol-DBU mixture then was added to the divinyl sulfone-alcohol mixture and stirred for 30 sec at room temperature while viscosity increased. The viscous mixture was poured into a Teflon® mold and cured at 80 °C for 22 h.

Before reprocessing in the hot press, the material was put into the oven (140 °C) for 30 min to avoid post-curing in the hot press.

Figure S37. Pictures of **poly4** after curing at 80 °C.

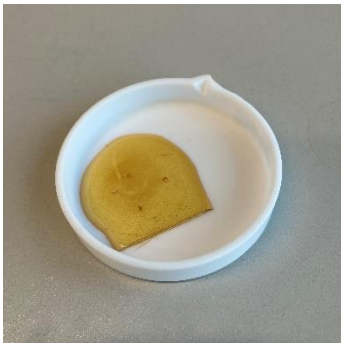


Figure S38. Pictures of **poly4** after curing at 140 °C.

Swelling test and sol-gel analysis

A square (size = 10.8 mm × 10.3 mm × 2.1 mm, mass = 295.5 mg) was cut from the sample and immersed in 8 mL methylene chloride for 22 h. Due to solvent uptake, the square increased to 14.0 mm × 13.2 mm × 2.6 mm which is equivalent to a 106% increase in volume. A swelling degree in wt% could not be determined as methylene chloride continuously evaporated from the sample. For sol-gel analysis the methylene chloride was removed in vacuum and the residual fraction was analyzed. The soluble fraction (Figure S40) was 3.7 wt% (11.0 mg). Another sample (352 mg) was continuously extracted with methylene chloride using a Soxhlet extraction apparatus for 24 h. Upon removal of the solvent and drying of the residue a mass of 14.1 mg (4 wt%) was determined. Additionally, swelling tests were performed in dioxane and toluene, in which only 16% and 17% volume increase were noted respectively.

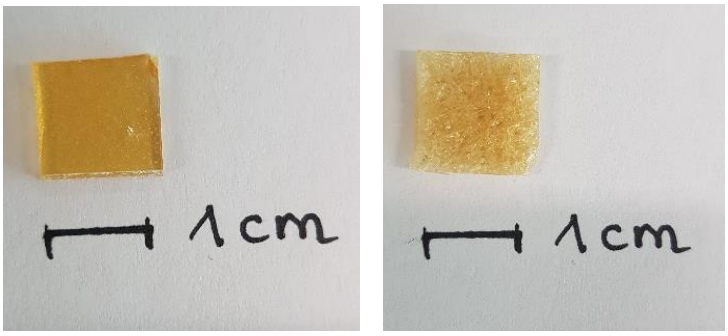


Figure S39. Pictures of **poly4** before and after immersion in methylene chloride for 22 h.

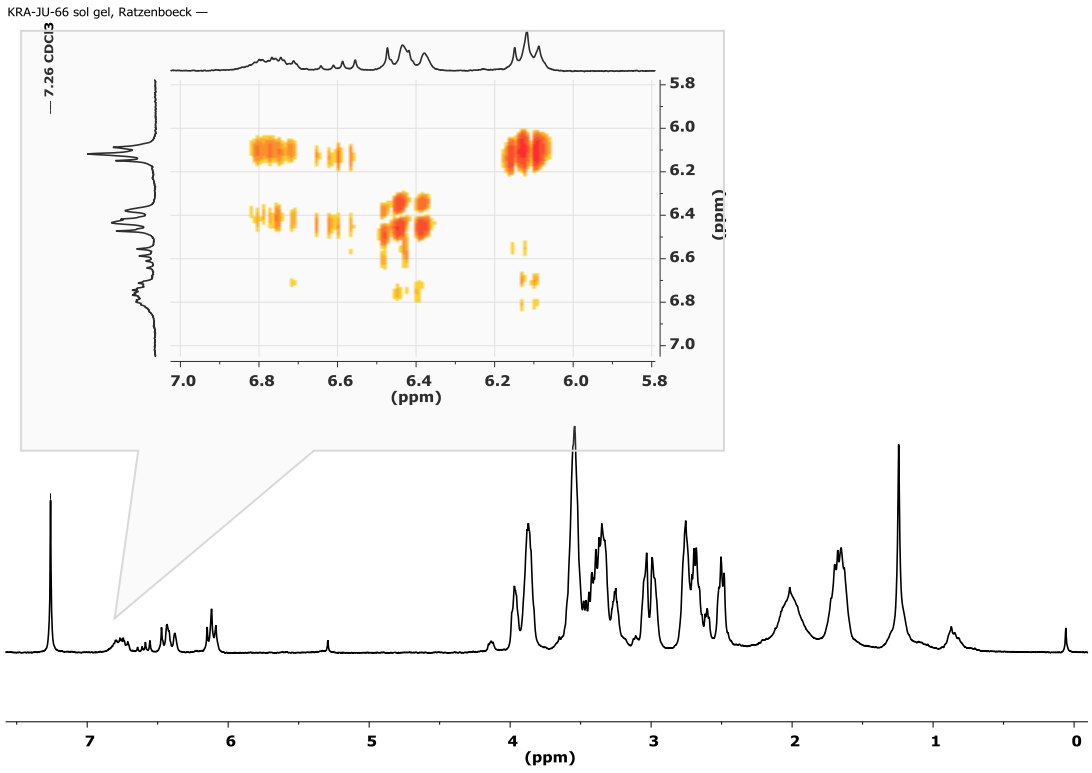


Figure S40. ^{1}H-NMR and ^{1}H-^{1}H COSY spectrum of soluble fracture of **poly4** in $CDCl_3$.

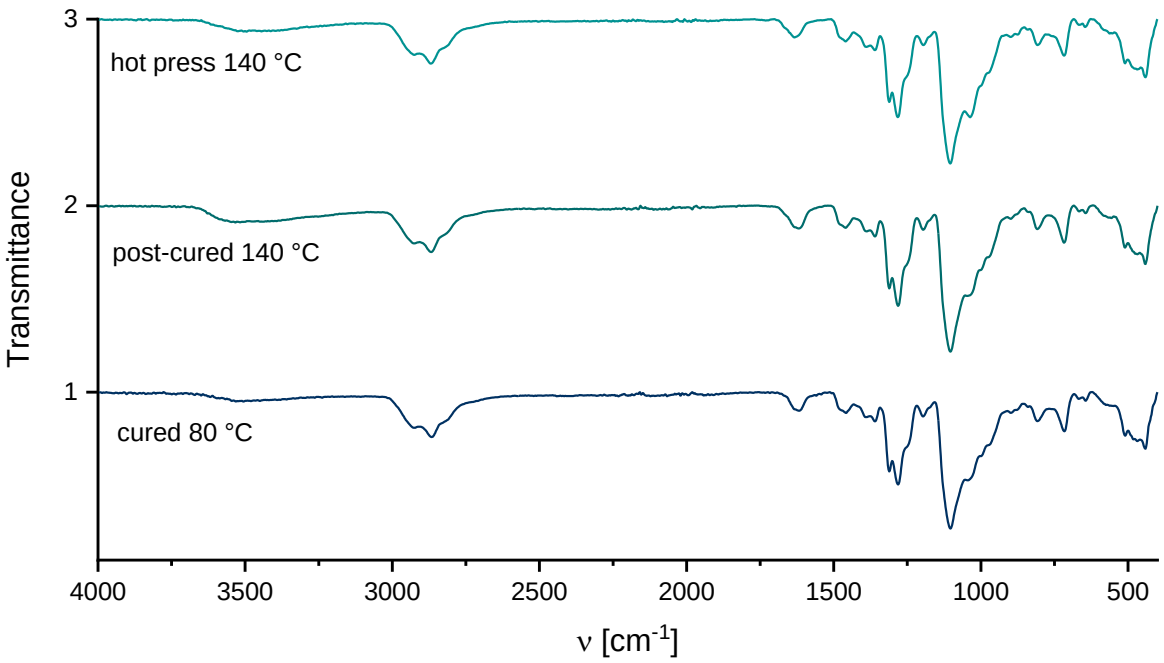


Figure S41. IR spectrum of **poly4** after curing at 80 °C, post-curing at 140 °C and hot press experiment at 140 °C.

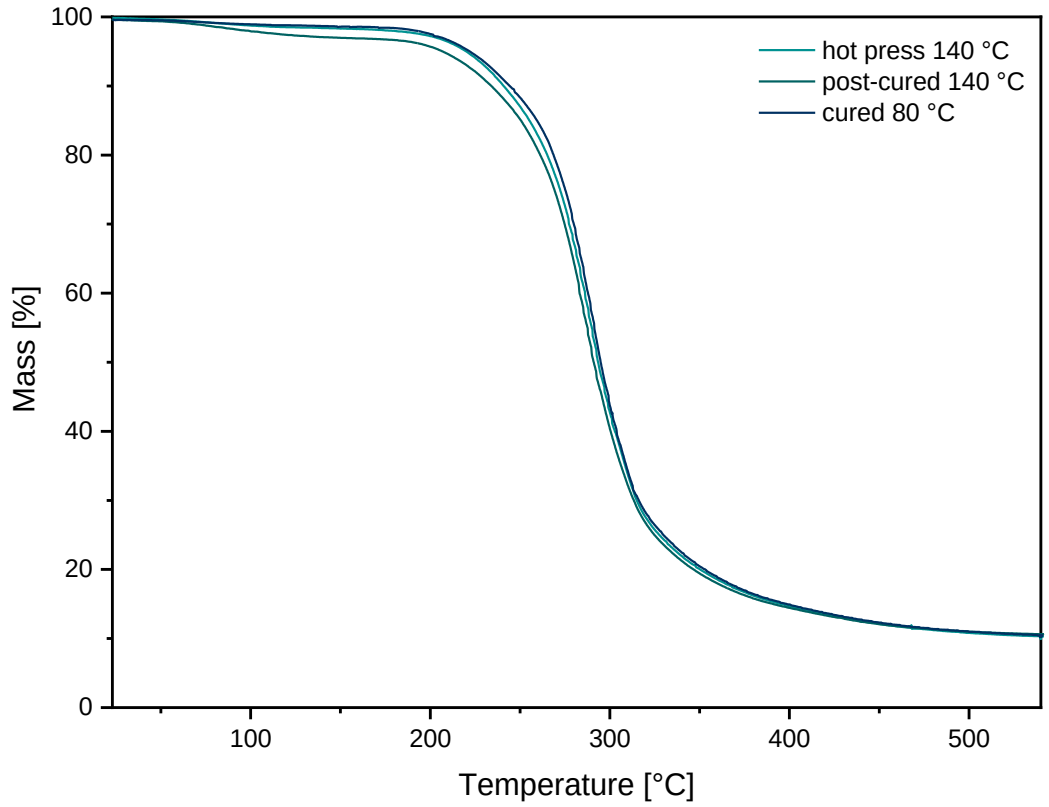


Figure S42. Thermogravimetric analysis of **poly4** after curing at 80 °C, post-curing at 140 °C and hot press experiment at 140 °C.

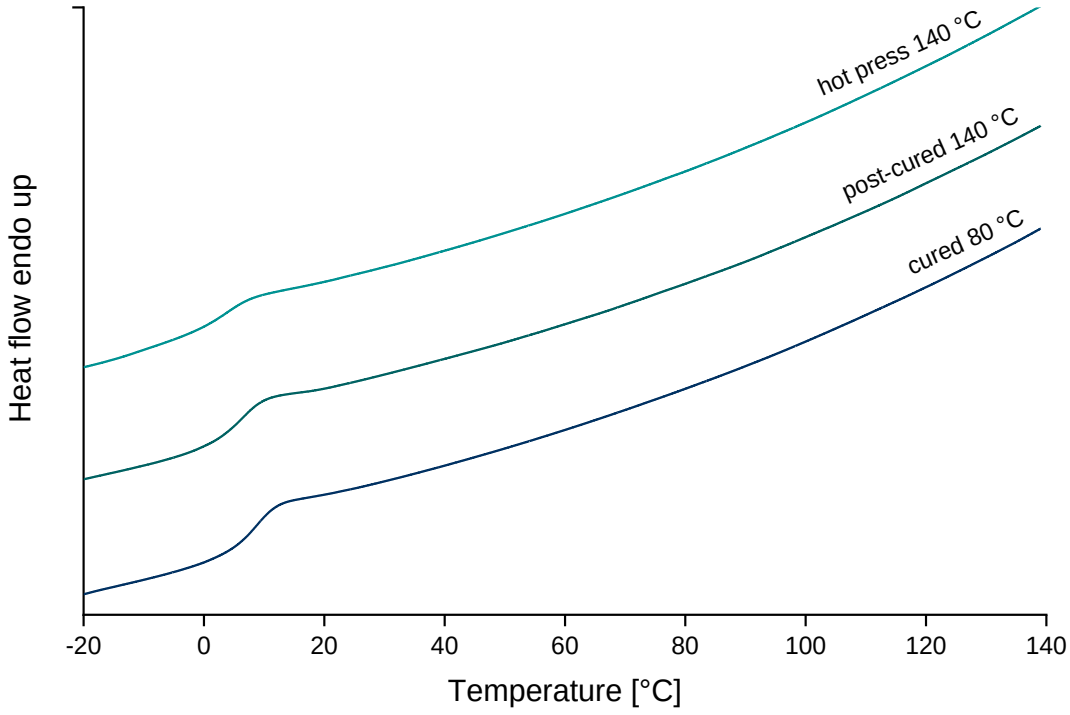


Figure S43. DSC curves of 3rd heat run (heating rate of 40 °C/min) of **poly4** after curing at 80 °C, post-curing at 140 °C and hot press experiment at 140 °C

Table S7: Glass transition temperature (T_g) of **poly4** taken from 3rd heat run (heating rate of 40 °C/min) in DSC measurements and degradation onset temperature ($T_{d\,95\%}$) determined by TGA.

Sample	T_g [°C]	$T_{d\,95\%}$ [°C]
poly4 cured at 80 °C	8	222
poly4 post-cured at 140 °C	5	207
poly4 hot press 140°C	3	220

Hot press reprocessing

For reprocessing the laboratory platen press P 200 PV from Collin was used. The material was cut into small pieces (3-4 mm) and put into a round mold (Ø = 2.5 cm). The sample was then placed into the preheated oven (140 °C) and was pressed with 3 bar for 2 min. Thereafter, the pressure was increased to 50 bar and kept constant for 1 h. The sample was removed from the hot oven and taken out of the mold while still being warm.

The obtained sample was again cut into small pieces, put into the mold and pressed in the hot press as mentioned above. The procedure was in total repeated three times.

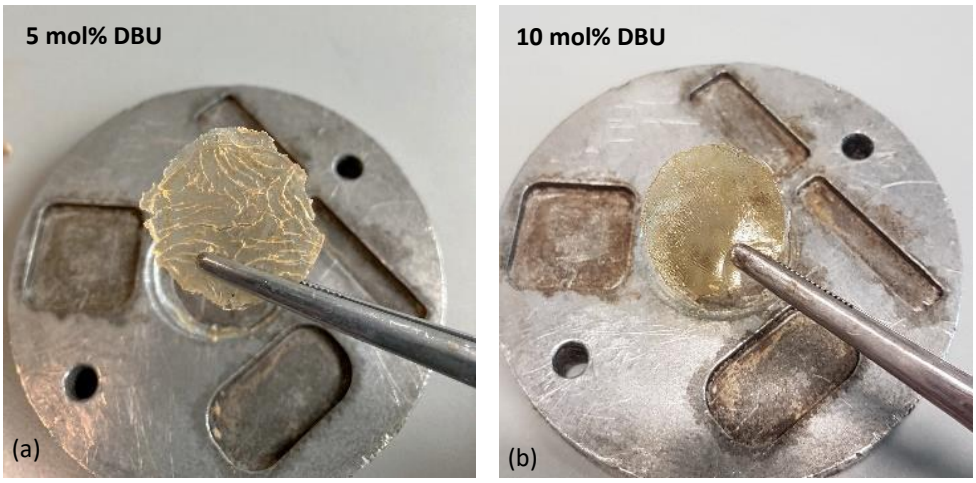


Figure S44. Pictures of **poly4** prepared with (a) 5 mol% DBU vs (b) 10 mol% DBU after hot press (1 h, 140 °C, 50 bar).

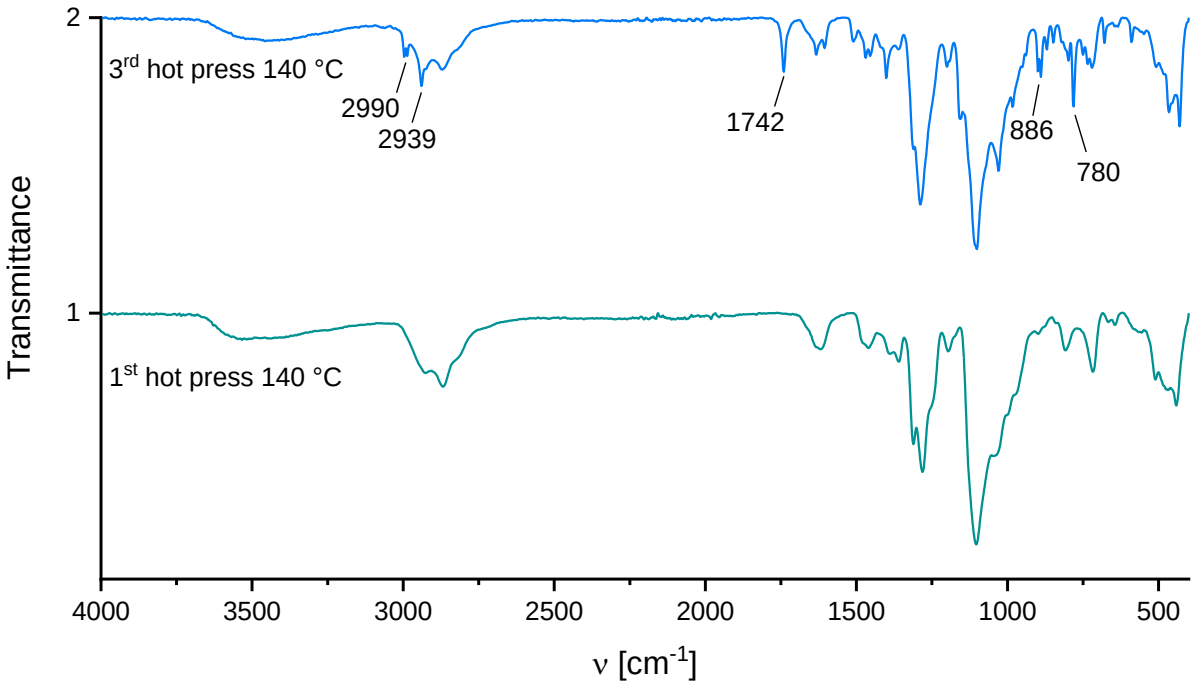


Figure S45. IR spectrum of **poly4** after the first (bottom) and third (top) time in the hot press at 140 °C.

Rheology

Samples for rheology were prepared by pouring the reaction mixture on a Teflon® plate before curing them at 80°C for 22 h followed by an additional curing step at 140 °C for 30 min. Uniform, rectangular samples with a width and length of about 10 mm and a thickness 1.8 ± 0.2 mm were cut out. For details on the stress relaxation experiments see General Information.

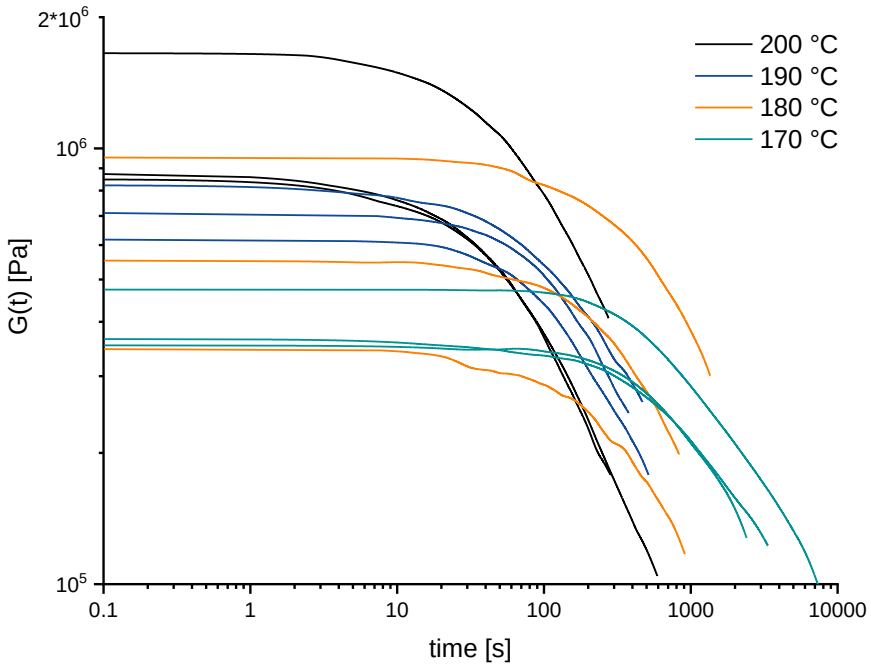


Figure S46. Non-normalized stress relaxation experiment at 170, 180, 190, and 200 °C in triple determination; parallel plate setup ø = 8 mm; preset F_n = 1 N; strain = 1%.

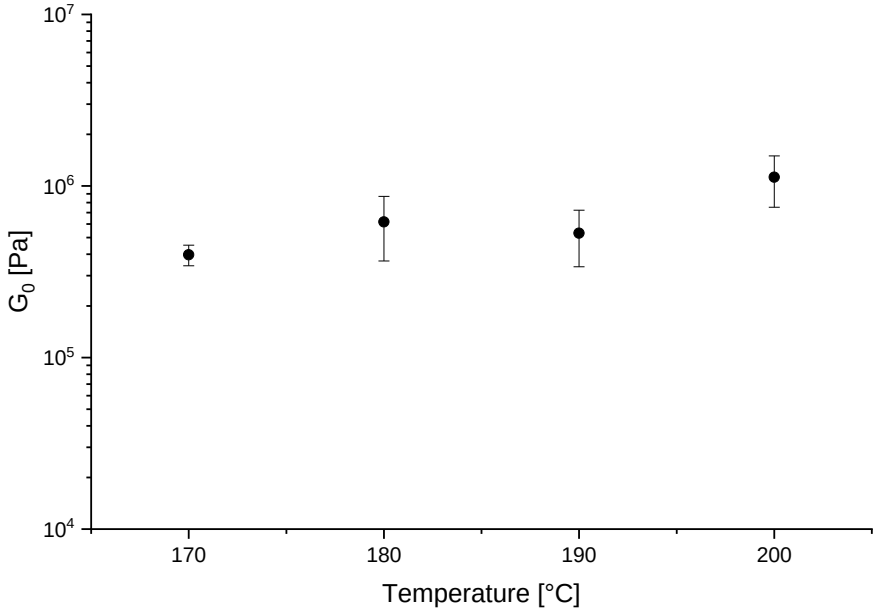


Figure S47. Temperature dependence of initial stress relaxation modulus G_0 at t = 0.1 s; parallel plate setup ø = 8 mm; preset F_n = 1 N; strain = 1%.

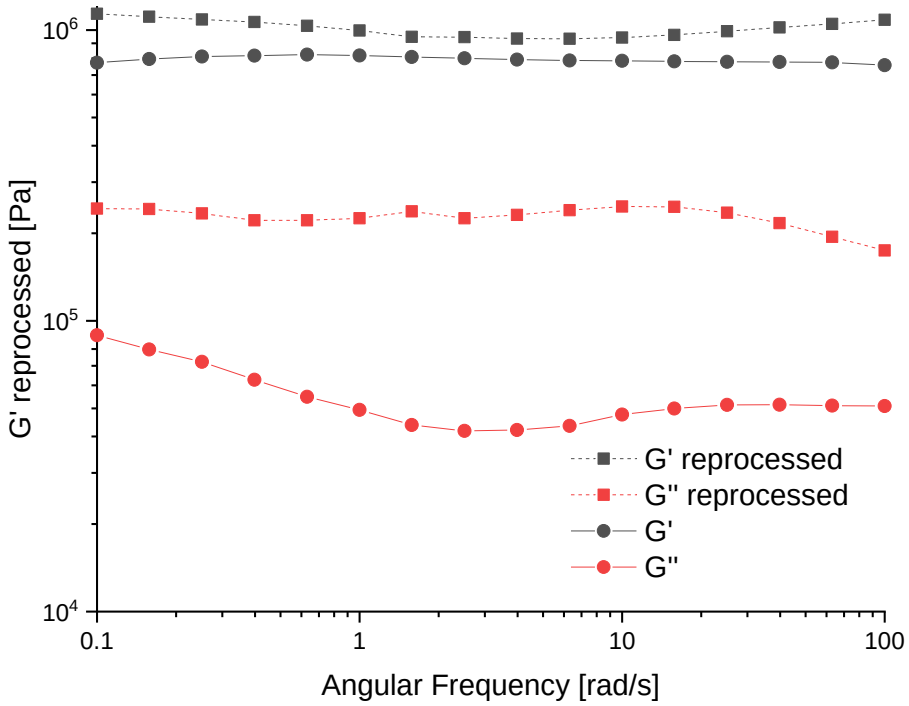


Figure S48. Frequency sweep at 180 °C showing storage (G‘) and loss modulus (G’’) of the sample before and after reprocessing at 180 °C in a range of 0.1-100 rad/s.

References

[1] S. M. Fischer, S. Renner, A. D. Boese, C. Slugovc, Electron-rich triarylphosphines as nucleophilic catalysts for oxa-Michael reactions, *Beilstein J. Org. Chem.* **2021**, *17*, 1689–1697. DOI 10.3762/bjoc.17.117

[2] COSMO-conf 4.3, COSMOlogic GmbH & Co KG: Leverkusen, Germany, **2013**.

[3] J. P. Perdew, K. Burke, M. Ernzerhof, Generalized Gradient Approximation Made Simple, *Phys. Rev. Lett.* **1996**, *77*, 3865–3868. DOI: 10.1103/PhysRevLett.77.3865

[4] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, A Consistent and Accurate Ab Initio Parametrization of Density Functional Dispersion Correction (DFT-D) for the 94 Elements H-Pu, *J. Chem. Phys.* **2010**, *132*, 154104. DOI: 10.1063/1.3382344

[5] F. Neese, Software Update: The ORCA Program System, Version 4.0., *Wiley Interdiscip. Rev. Comput. Mol. Sci*. **2018**, *8*, e1327. DOI: 10.1002/WCMS.1327

[6] S. Grimme, Semiempirical hybrid density functional with perturbative second-order correlation, *J. Chem. Phys.*, **2006**, *124*, 0341081-03410816. DOI: 10.1063/1.2148954

[7] V. Barone, M. Cossi, Quantum Calculation of Molecular Energies and Energy Gradients in Solution by a Conductor Solvent Model, *J. Phys. Chem. A*, **1998**, *102*, 1996-2001. DOI: 10.1021/jp9716997

[8] S. Strasser, C. Wappl, C. Slugovc, Solvent-free macrocyclisation by nucleophile-mediated oxa-Michael addition polymerisation of divinyl sulfone and alcohols, *Polym. Chem.* **2017**, *8*, 1797–1804. DOI 10.1039/C7PY00152E

[9] G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, K. I. Goldberg, NMR Chemical Shifts of Trace Impurities: Common Laboratory Solvents, Organics, and Gases in Deuterated Solvents Relevant to the Organometallic Chemist, *Organometallics* **2010**, *29*, 2176-2179. DOI: 10.1021/om100106e