Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supplementary Information

Sequential dual-curing of electron-deficient olefins and alcohols relying on oxa-Michael addition and anionic polymerization

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Contents

1 General Information

All experiments were performed under ambient conditions. Chemicals were purchased from Sigma Aldrich, Carl Roth, Merck or TCI and were used as received. Stabilizers present in the Michael acceptors were not removed. ^{1}H- and ^{13}C- NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer at 25 °C (^{1}H: 300.36 MHz; ^{13}C: 75.53 MHz). Chemical shifts δ are given in ppm relative to the residual protons and carbons of the deuterated solvent. ($CHCl_3$: 7.26 ppm and 77.16 ppm, DMSO: 2.50 and 39.52 for ^{1}H and ^{13}C, respectively). ^{31}P measurements were performed on a Varian Inova 500 MHz instrument operating at 202.547 MHz. Chemical shifts are reported in ppm relative to an external standard (85 % H_3PO_4). Spectra are ^{1}H-decoupled and as delay time (d1) 25 s was set. Deuterated solvents were obtained from Cambridge Isotope Laboratories Inc. Size exclusion chromatography (SEC) was performed on a system provided by Shimadzu (equipped with two separating columns from MZ-Gel SD plus, 500 A and 100 A, linear 5µ; 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. Additionally, SEC measurements were performed on a machine by Knauer, equipped with two separating columns from AppliChrom (500 A and 100 A, linear 5µ, 300x8 mm) and an RI detector (Azura RID 2.1L) using THF as eluent.

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·min^{-1} was used in combination with a protective flow of helium of 10 mL·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.

2 Lewis-base catalyzed anionic polymerization of electron-deficient olefins

2.1 Polymerization of methyl acrylate

Methyl acrylate was mixed with 5 mol% catalyst (DMAP, DBU, TMG, TPP, TMTPP, TTMPP, P_2-tBu) and the reaction mixture was stirred at 60°C for 24 hours. After 1 h and 24 h aliquots of the reaction mixture were sampled and subjected to NMR spectroscopy. Poly(methyl acrylate) formed in the TTMPP and P_2-tBu (full conversion of methyl acrylate after 1h) catalyzed reactions. For TMTPP, after 24 h, 32 % of dimethyl 2-methylenepentanedioate has formed. For the other catalysts, no conversion could be observed after 24 h.

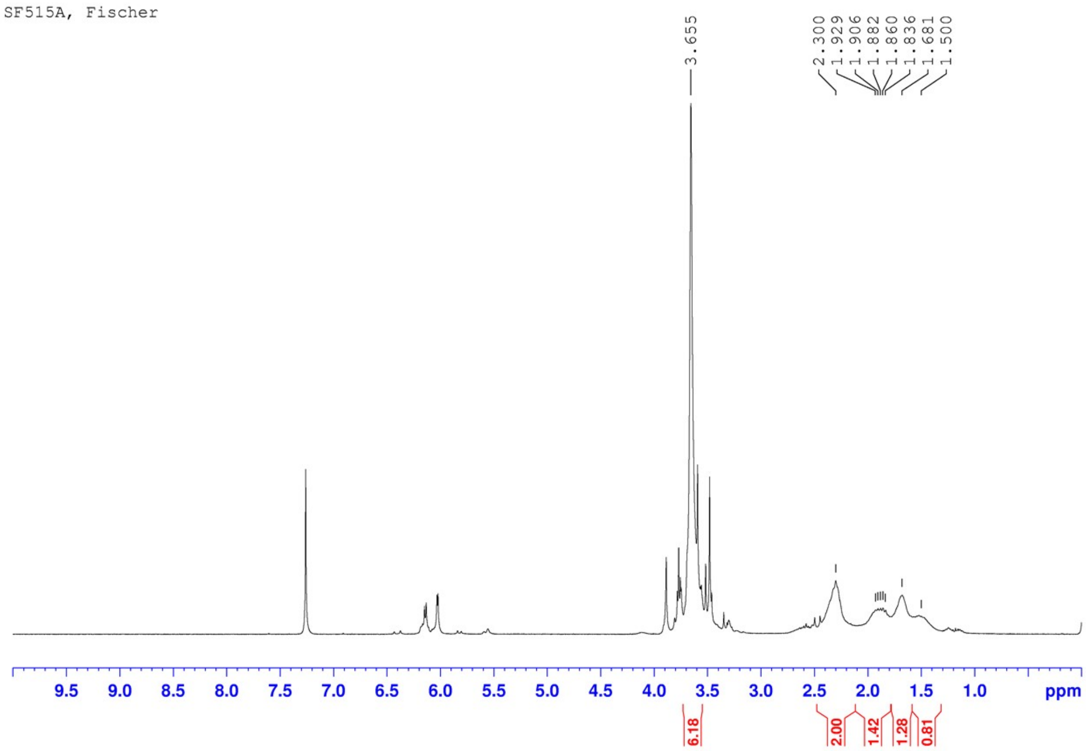


Figure S1 ^{1}H-NMR spectrum (300 MHz, $CDCl_3$) of the reaction mixture of methyl acrylate and 5 mol% TTMPP after 24 h at 60°C

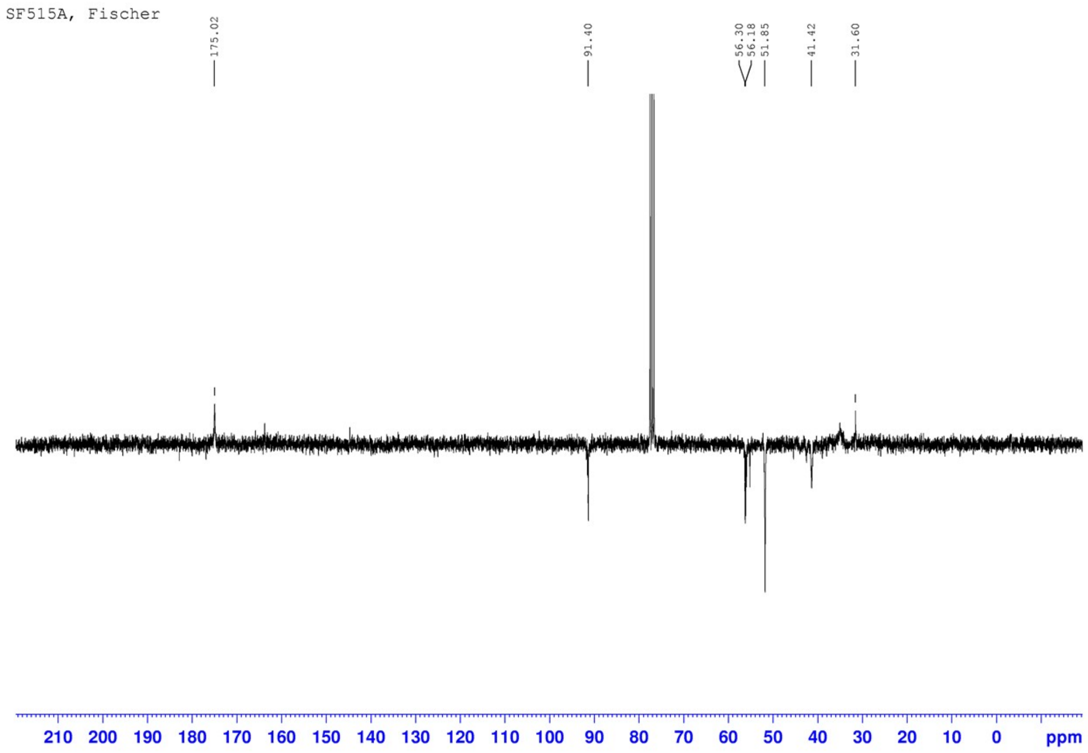


Figure S2 ^{13}C-APT spectrum (75.53 MHz, $CDCl_3$) of the reaction mixture of methyl acrylate and 5 mol% TTMPP after 24 h at 60 °C

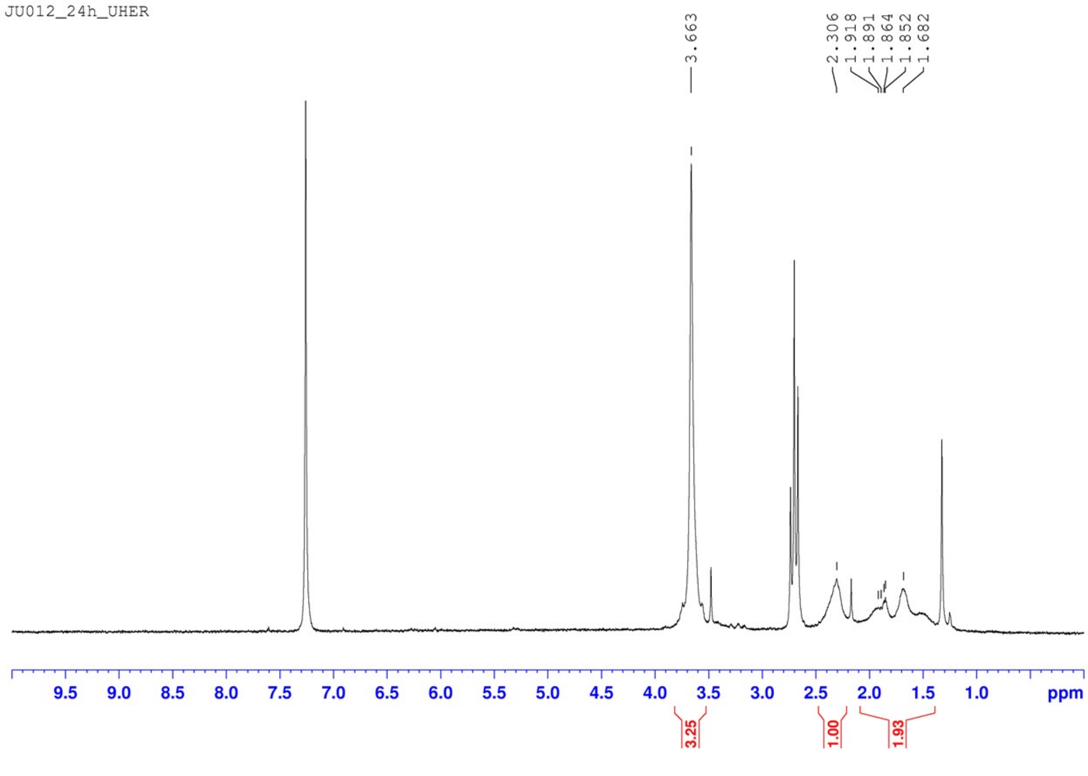


Figure S3 ^{1}H-NMR spectrum (300 MHz, $CDCl_3$) of the reaction mixture of methyl acrylate and 5 mol% P2-tBu after 24 h at 60°C

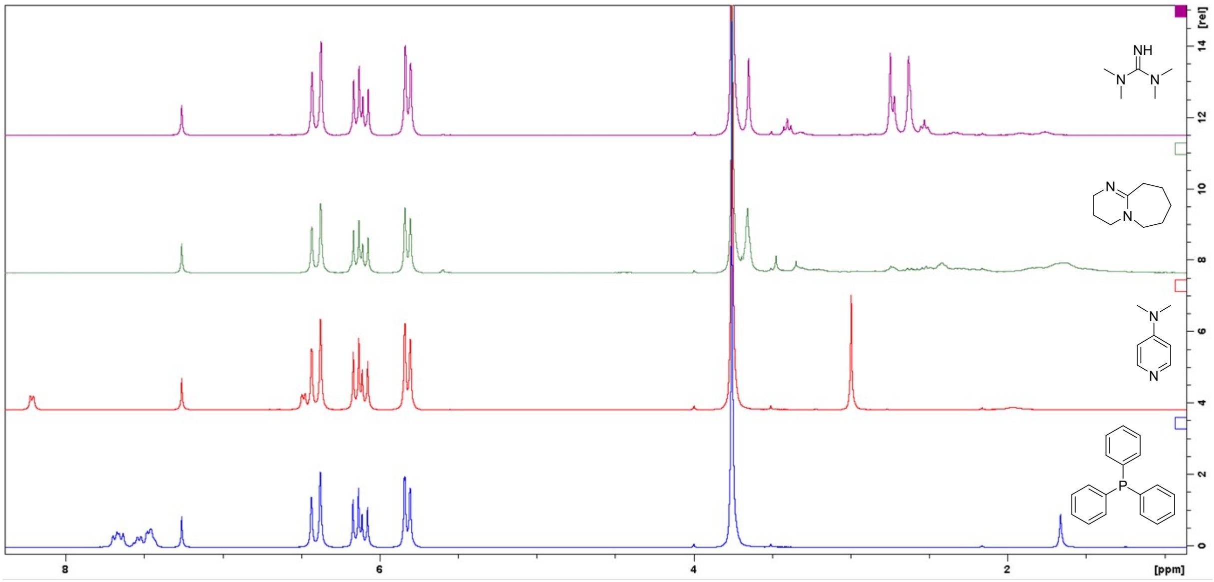


Figure S4 ^1H-NMR spectra (300 MHz, $CDCl_3$) of the reaction mixture of methyl acrylate and 5 mol% TMG (purple), DBU (green), DMAP (red) and triphenylphosphine (blue) after 24 h at 60 °C

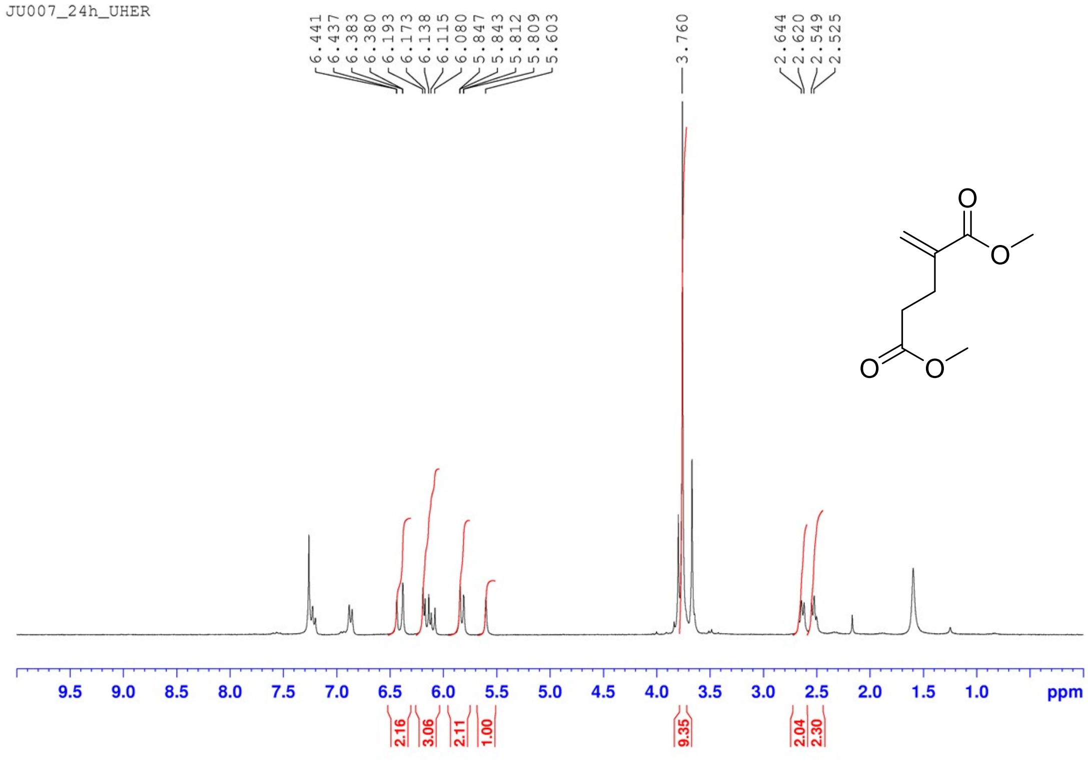


Figure S5 ^1H-NMR spectrum (300 MHz, $CDCl_3$) of the reaction mixture of methyl acrylate and 5 mol% TMPP after 24 h at 60°C

Table S1 SEC analysis of poly(methyl acrylate) obtained under different conditions

Catalyst	Loading [mol%]	Temp [°C]	Mn (PDI)
TTMPP	5	60	2100 (2.0)
TTMPP	2.5	60	2200 (2.1)
P2-tBu	5	60	3700 (2.6)

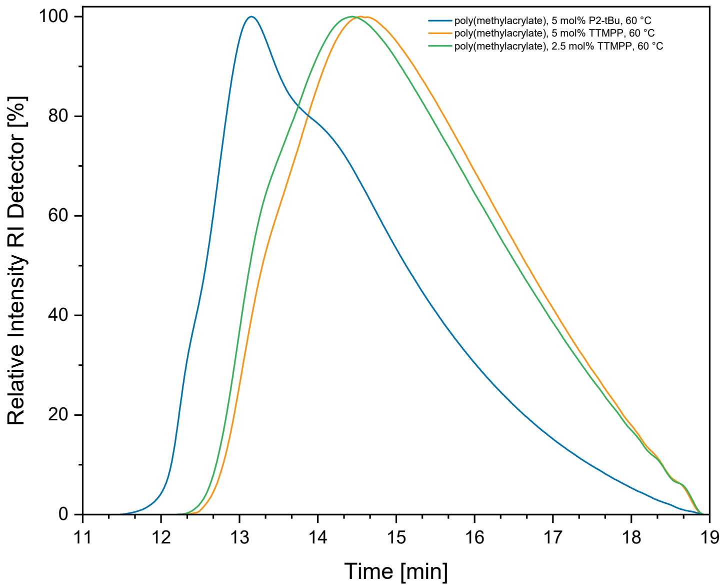


Figure S6 Size exclusion chromatograms (in THF, relative to poly(styrene) standards), of poly(methylacrylate), prepared with TTMPP or P2-tBu in different catalytic loadings using a reaction time of 24 h and a reaction temperature of 60 °C

2.2 Polymerization of ethyl acrylate

Ethyl acrylate was mixed with 5 mol% TTMPP and the reaction mixture was stirred for 24 hours at 60°C. A sticky, white polymer was obtained. Average molecular weight (Mn) of 3670 g/mol (PDI: 2.6) was determined.

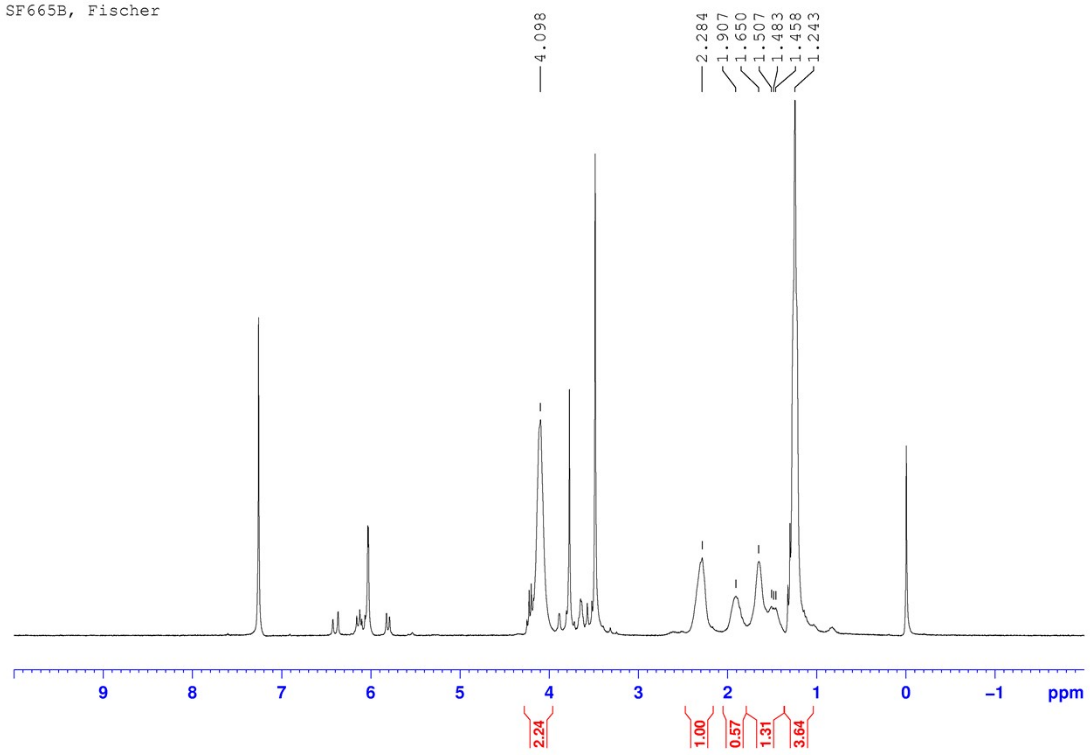


Figure S7 ^{1}H-NMR spectrum (300 MHz, $CDCl_3$) of the reaction mixture of ethyl acrylate and 5 mol% P_2-tBu after 24 h at 60 °C

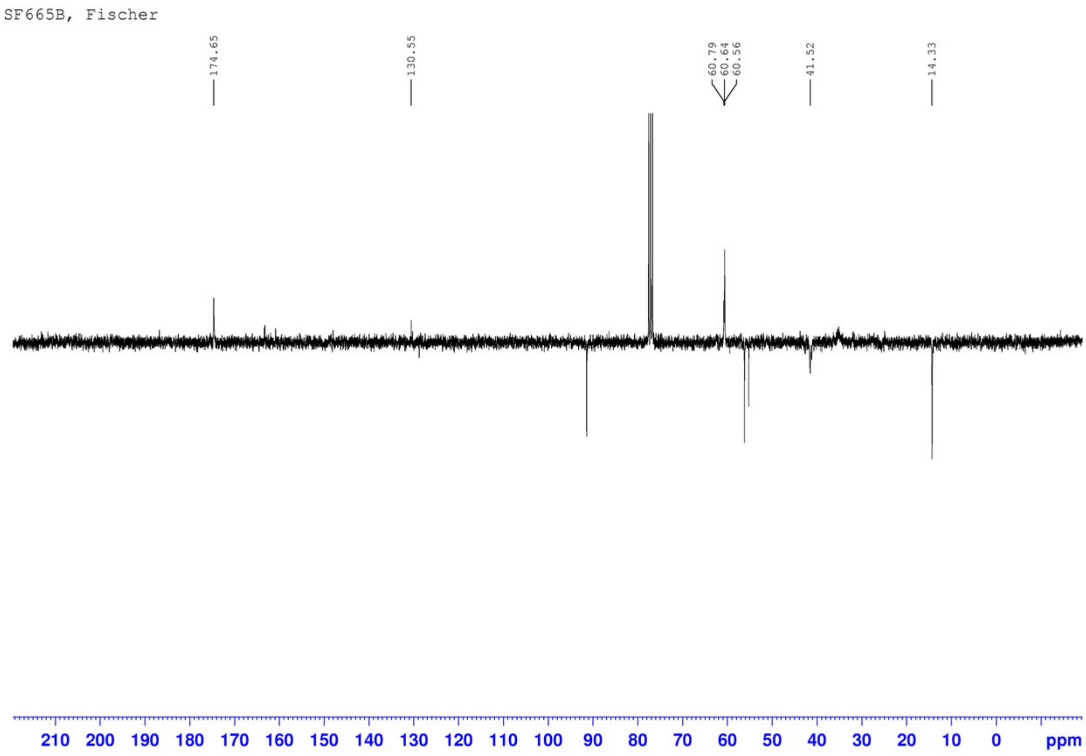


Figure S8 ^{13}C-APT spectrum (75.53 MHz, CDCl$_3$) of the reaction mixture of ethyl acrylate and 5 mol% TTMPP after 24 h at 60°C

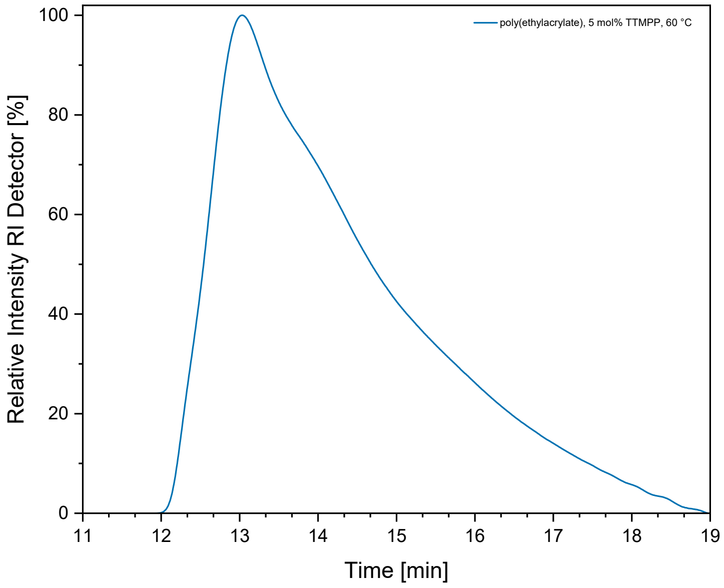


Figure S9 Size exclusion chromatograms (in THF, relative to poly(styrene) standards), of poly(ethylacrylate), prepared with 5 mol% TTMPP using a reaction time of 24 h and a reaction temperature of 60 °C

2.3 Polymerization of benzyl acrylate

Benzyl acrylate was mixed with 5 mol% TTMPP and the reaction mixture was stirred for 24 hours at 60°C. A sticky, white polymer was obtained.

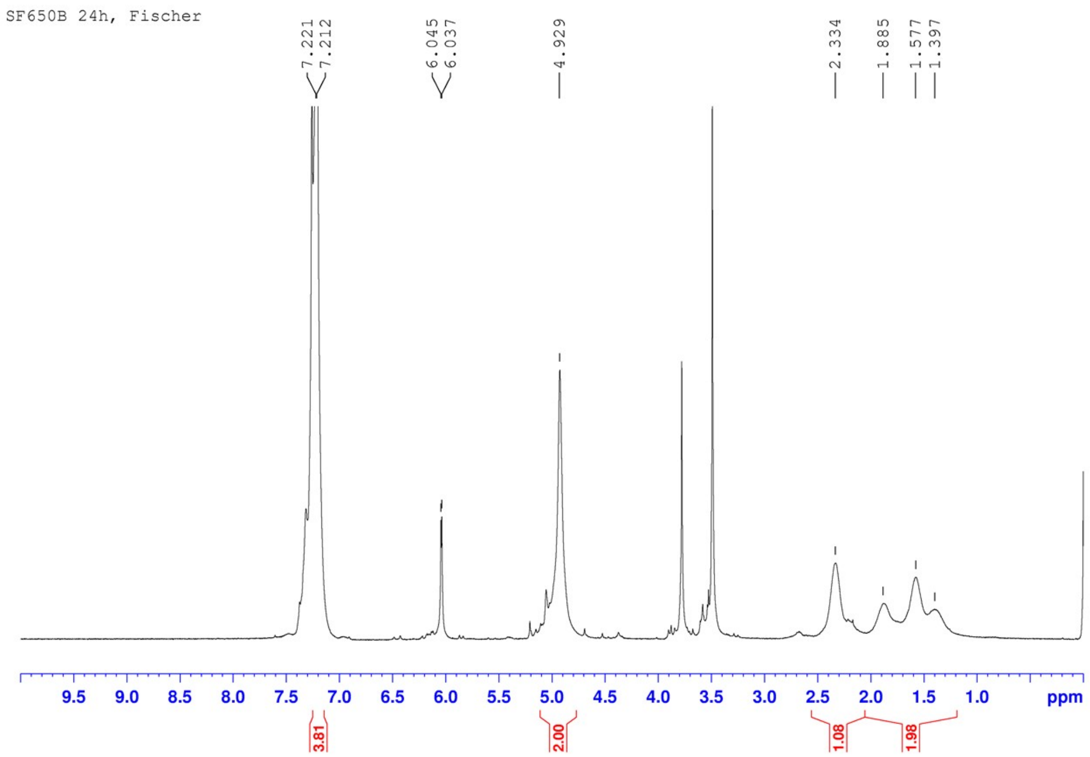


Figure S10 ^{1}H-NMR spectrum (300 MHz, $CDCl_3$) of the reaction mixture of benzyl acrylate and 5 mol% P_2-tBu after 24 h at 60°C

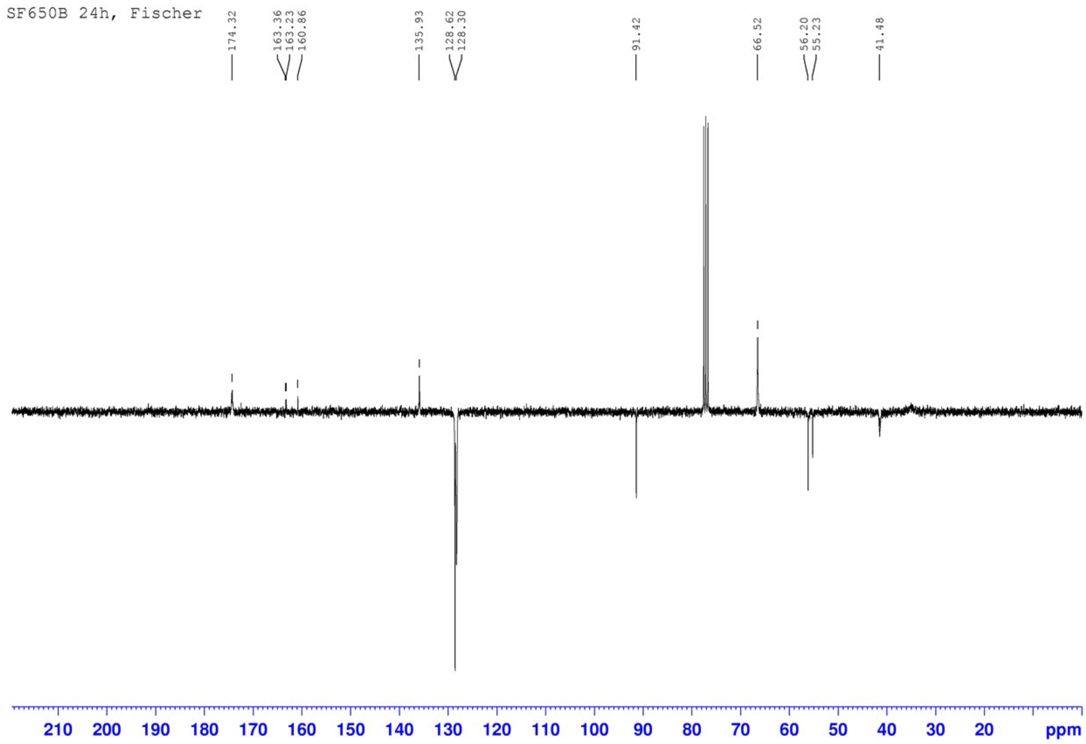


Figure S11 ^{13}C-APT spectrum (75.53 MHz, $CDCl_3$) of the reaction mixture of benzyl acrylate and 5 mol% TTMPP after 24 h at 60°C

Methyl crotonate and methyl methacrylate could not be polymerized under these conditions.

2.4 Multifunctional acrylates

2.4.1 Butanediol diacrylate (BDDA)

BDDA was mixed with 5 mol% TTMPP or P_2-tBu and the reaction mixture was stirred at 60 °C for 24 h.

Table S2 Overview of screened reaction conditions for the anionic polymerization of BDDA

Catalyst	Loading [mol%]	Temp [°C]	Soluble fraction
TTMPP	10	60	TTMPP
TTMPP	5	60	Nothing extractable
TTMPP	2.5	60	BDDA + TTMPP
TTMPP	5	25	BDDA + TTMPP

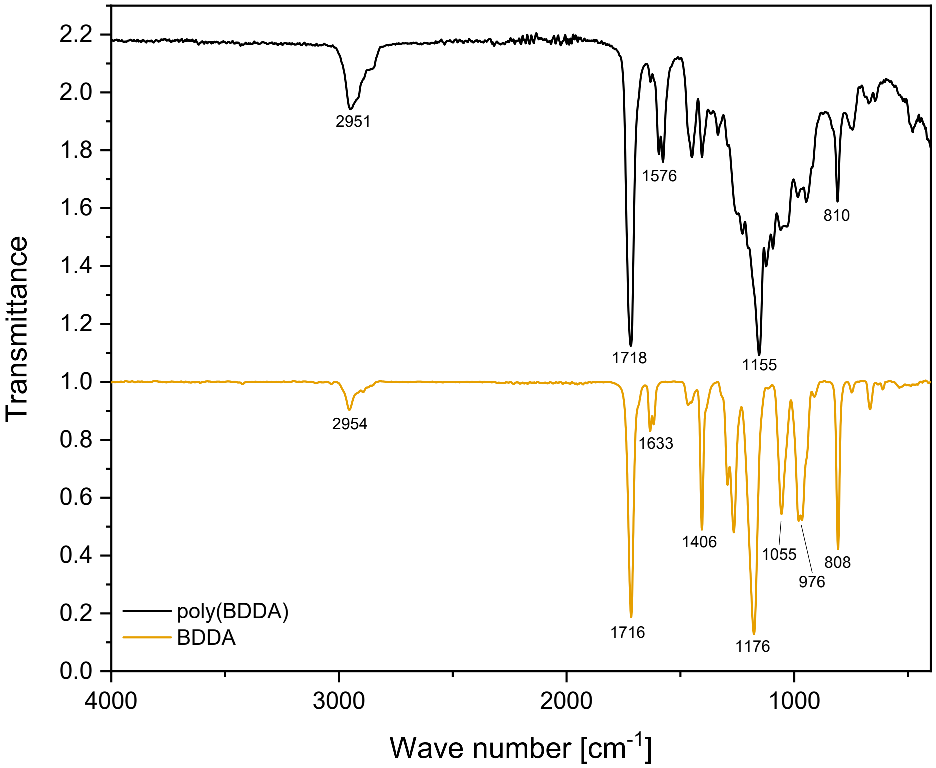


Figure S12 ATR-IR spectra of BDDA and poly(BDDA) with 5 mol% TTMPP

2.4.2 Trimethylolpropane triacrylate (TMPTA)

TMPTA (0.2 g, 0.68 mmol) was mixed with TTMPP (37.70 mg, 0.07 mmol, 0.1 equiv.) in a glass vial and the reaction mixture was stirred at 60 °C. After the initiator has fully dissolved (15 min), the reaction mixture solidified and a transparent, glass-like polymer was obtained. The polymer was moulded and extracted with chloroform. The solid was filtered off and the solvent was removed with a nitrogen stream. Small amounts of unreacted TMPTA as well as TTMPP could be recovered (Figure S13). Soluble fraction: 14.06 mg (7.4 %).

It was also attempted to perform the polymerization with 5 mol% catalyst, but no solid material could be obtained.

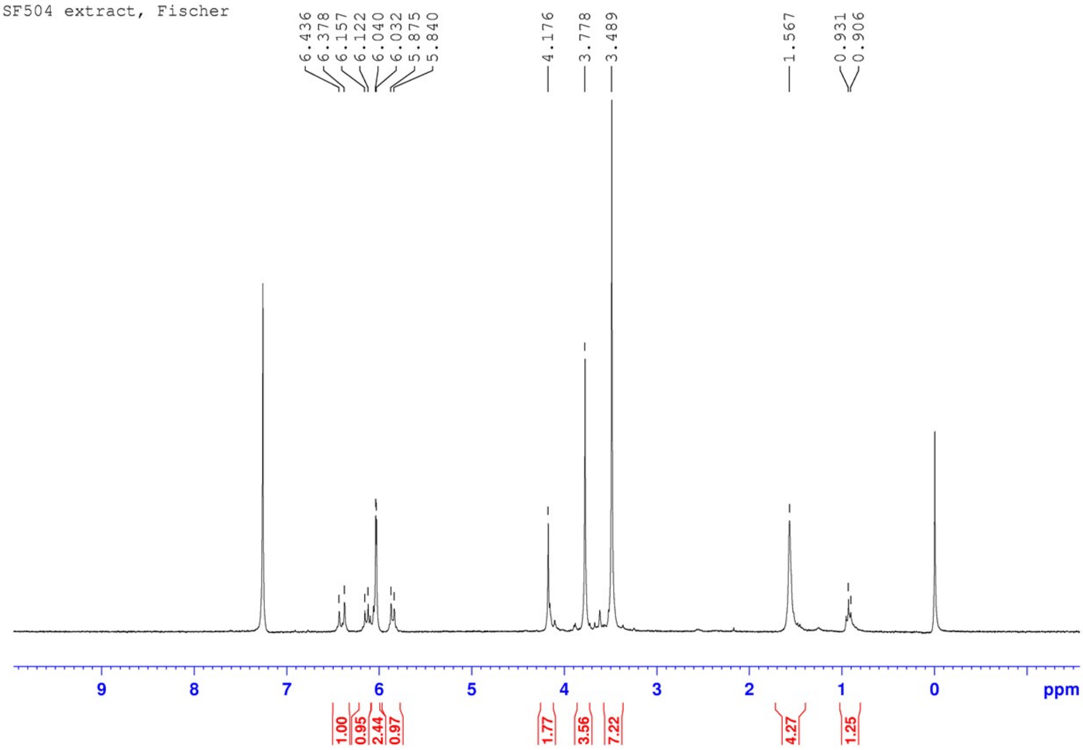


Figure S13 ^{1}H-NMR spectrum (300 MHz, $CDCl_3$) of the soluble fraction of poly(TMPTA) extracted with chloroform

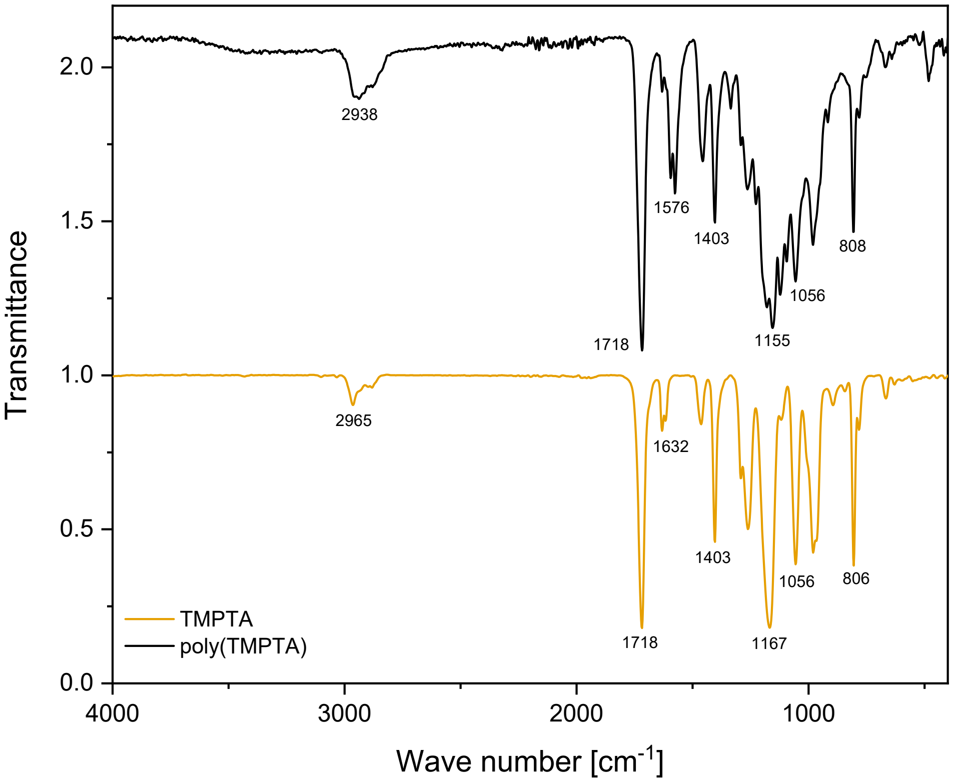


Figure S14 ATR-IR spectra of trimethylolpropane triacrylate and its polymer with 5 mol% TTMPP

The ATR-IR spectrum of poly(TMPTA) is characterized by a new band at 1575 and a broadening of the bands in the region of 1100-900 cm^{-1} (Figure S14).

2.5 Polymerization of divinyl sulfone

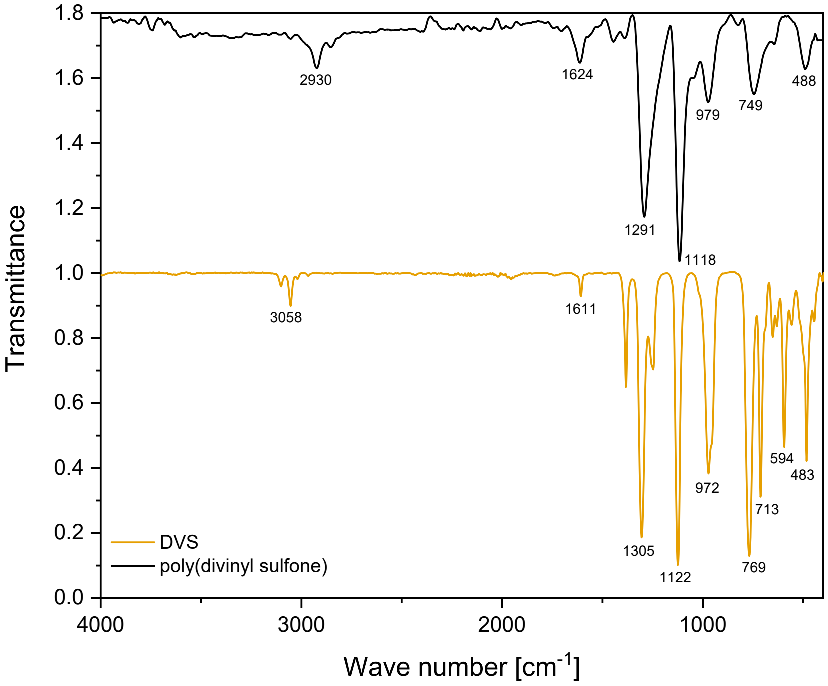


Figure S15 ATR-IR spectra of divinyl sulfone and poly(divinyl sulfone) with 5 mol% DBU

3 Model formulations for sequential polymerization

3.1 Reaction of methyl acrylate with substochiometric amounts of methanol

Methyl acrylate was reacted with 0.5 equiv. of methanol and 2.5 mol% TTMPP at 60 °C. Aliquots of the reaction mixture were sampled after 2, 5, 10, 30 and 60 min as well as after 2 h, 4 h and 24 h and subjected to NMR spectroscopy (Figure S16).

After 10 min, methanol was fully consumed and the oxa-Michael product has formed. Vinyl-coupling products started to form after 30 min when the alcohol was fully consumed. Methyl acrylate was fully consumed after 24 h (98.7 % double bond conversion). For details see Figure S17 and Figure S19.

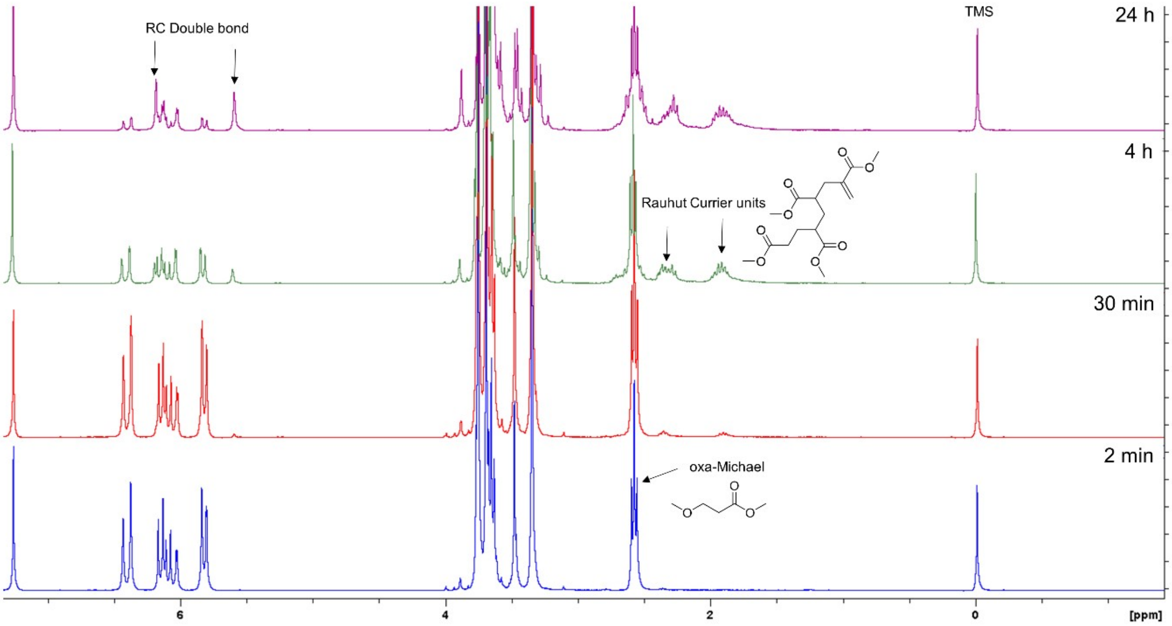


Figure S16 ^{1}H NMR spectra (300 MHz, $CDCl_3$) at various time intervals of the reaction mixture of methyl acrylate and 0.5 equiv. methanol with 2.5 mol% TTMPP at 60 °C

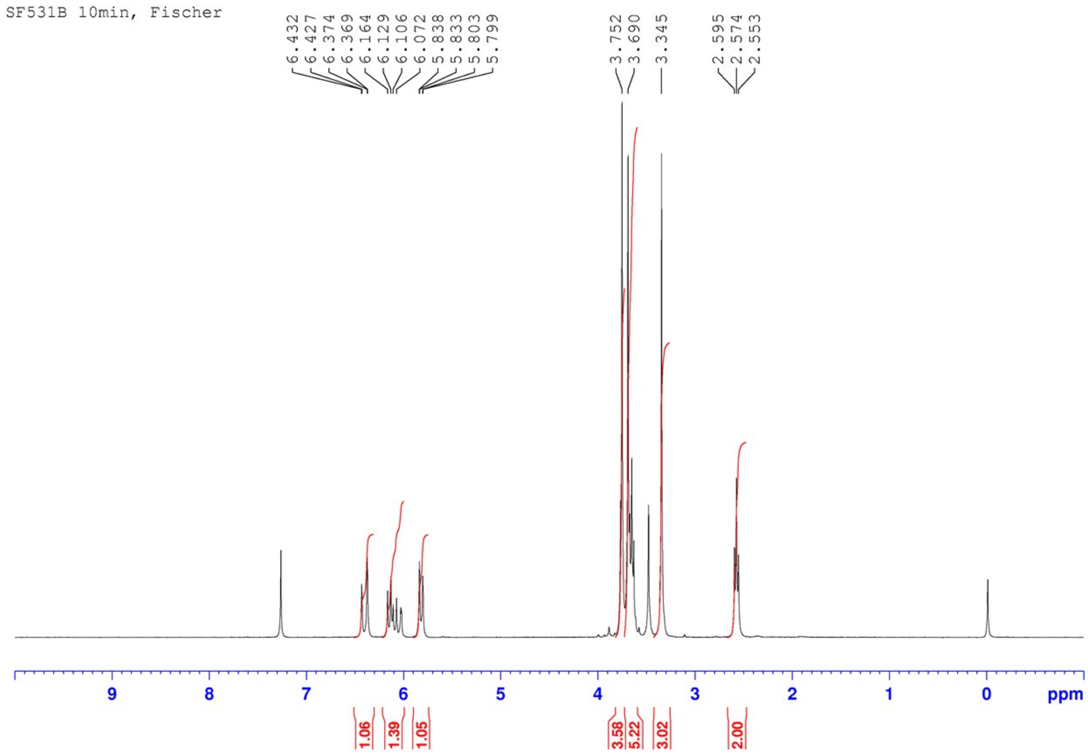


Figure S17 ^{1}H-NMR spectrum (300 MHz, $CDCl_3$) of the reaction mixture of methyl acrylate and 0.5 equiv. methanol with 2.5 mol% TTMPP as catalyst at 60 °C after 10 min

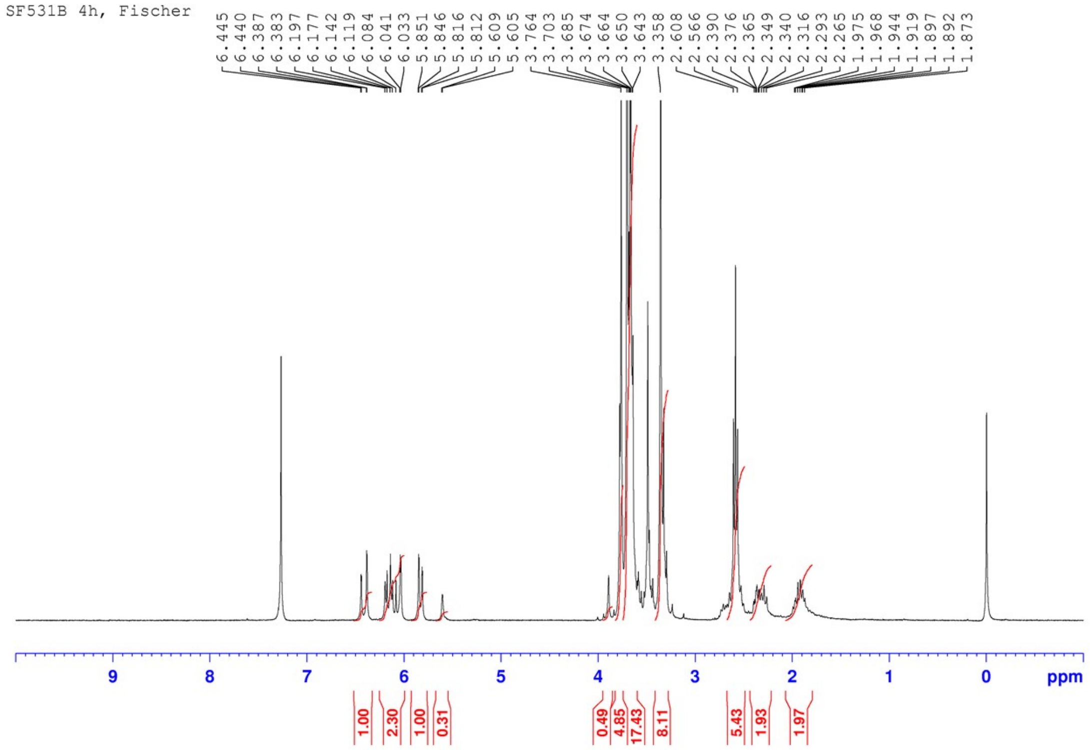


Figure S18 ^{1}H-NMR spectrum (300 MHz, $CDCl_3$) of the reaction mixture of methyl acrylate and 0.5 equiv. methanol with 2.5 mol% TTMPP as catalyst at 60 °C after 4 h

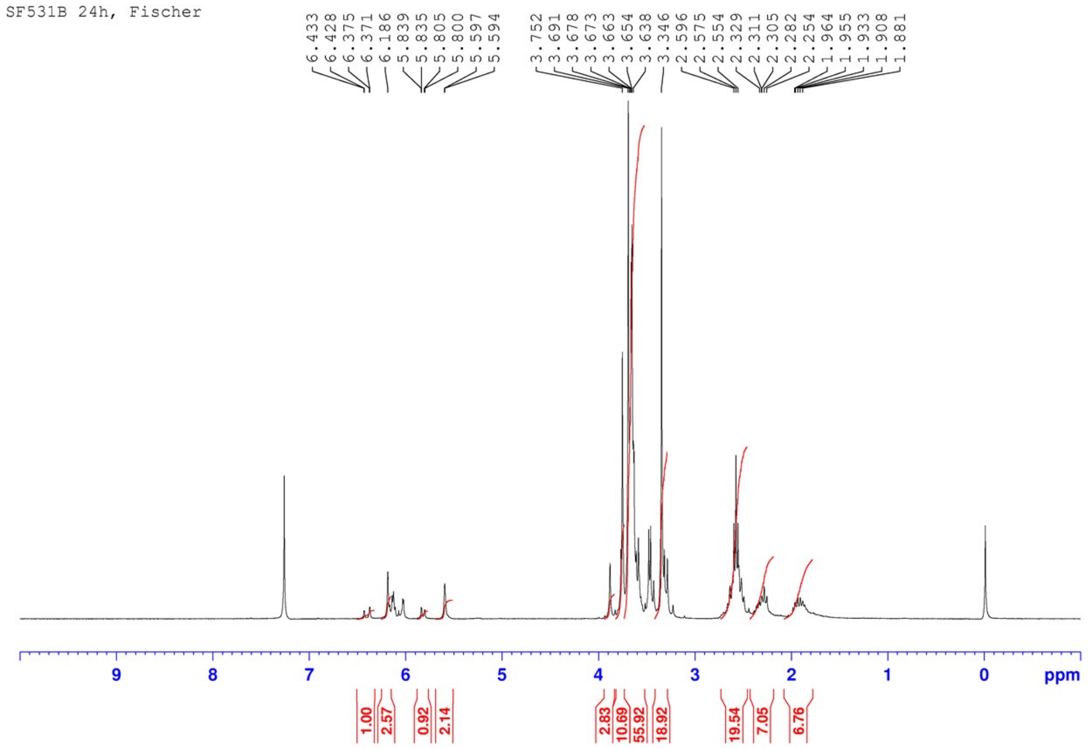
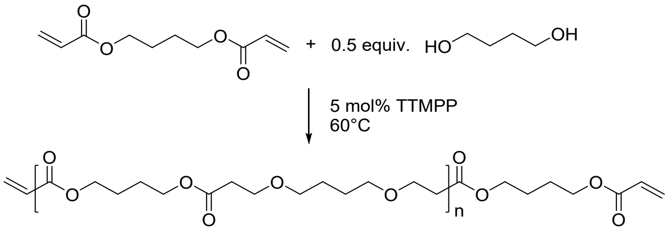


Figure S19 ^{1}H-NMR spectrum (300 MHz, $CDCl_3$) of the reaction mixture of methyl acrylate and 0.5 equiv. methanol with 2.5 mol% TTMPP as catalyst at 60 °C after 24 h

3.2 Reaction of butane-1,4-diol diacrylate and butane-1,4-diol (poly(BDDAcoBD$_{0.5}$))

The reaction of BDDA with 0.5 equiv. butane-1,4-diol and 5 mol% TTMPP as catalyst was followed via ^{1}H NMR spectroscopy. For this purpose, an aliquot of the reaction mixture was sampled after 15 min, 45 min and 1 h. After 15 min, 50 % of the acrylate groups have been consumed in oxa-Michael reactions and vinyl-terminated oligomers have formed (Figure S20).



Scheme S1 Oxa-Michael polymerization of butane-1,4-diol diacrylate and 0.5 equiv. butane-1,4-diol to form poly(BDDAcoBD$_{0.5}$)

After 45 minutes, the signals in NMR spectrum did not change significantly and also the viscosity of the reaction mixture remained similar. Overnight, the viscosity of the reaction mixture increased and a largely insoluble polymer was obtained. In the soluble fraction (^{1}H NMR spectrum in Figure S21) oligomers could be detected. The integral of the acrylate peak at 6.37 ppm has become smaller (1.68 vs 2.0) indicating that parts of the end groups were consumed in anionic polymerization.

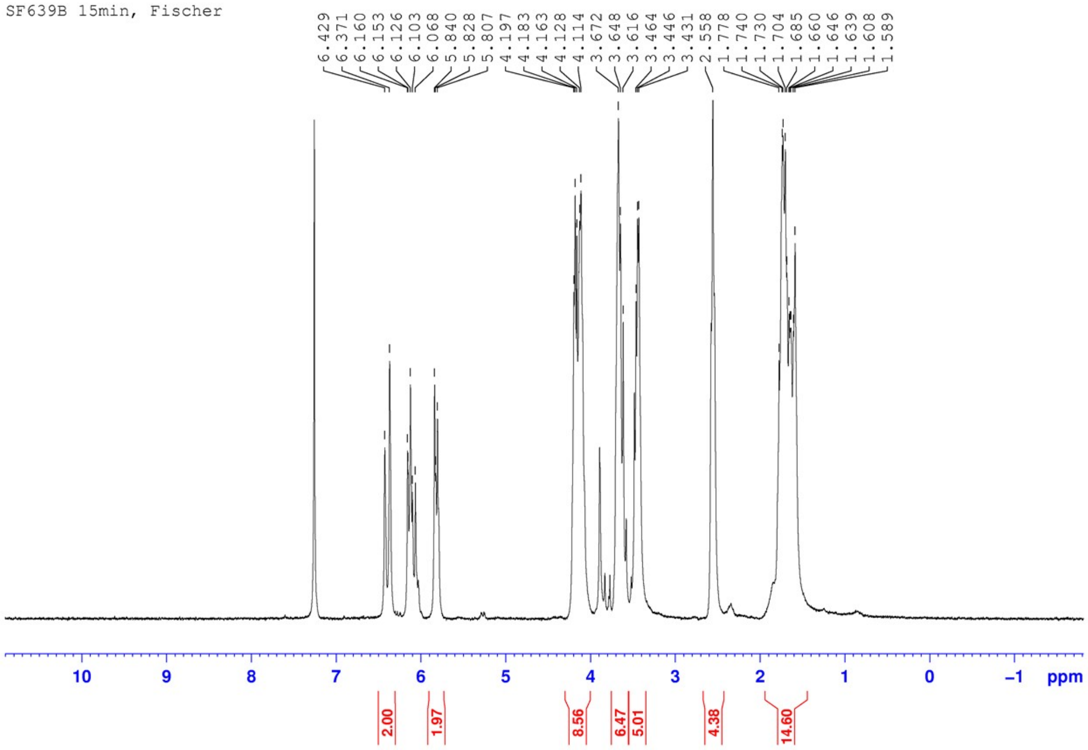


Figure S20 ^{1}H NMR spectrum (300 MHz, CDCl$_3$) of the reaction mixture of poly(BDDAcoBD$_{0.5}$) after 15 min reaction time

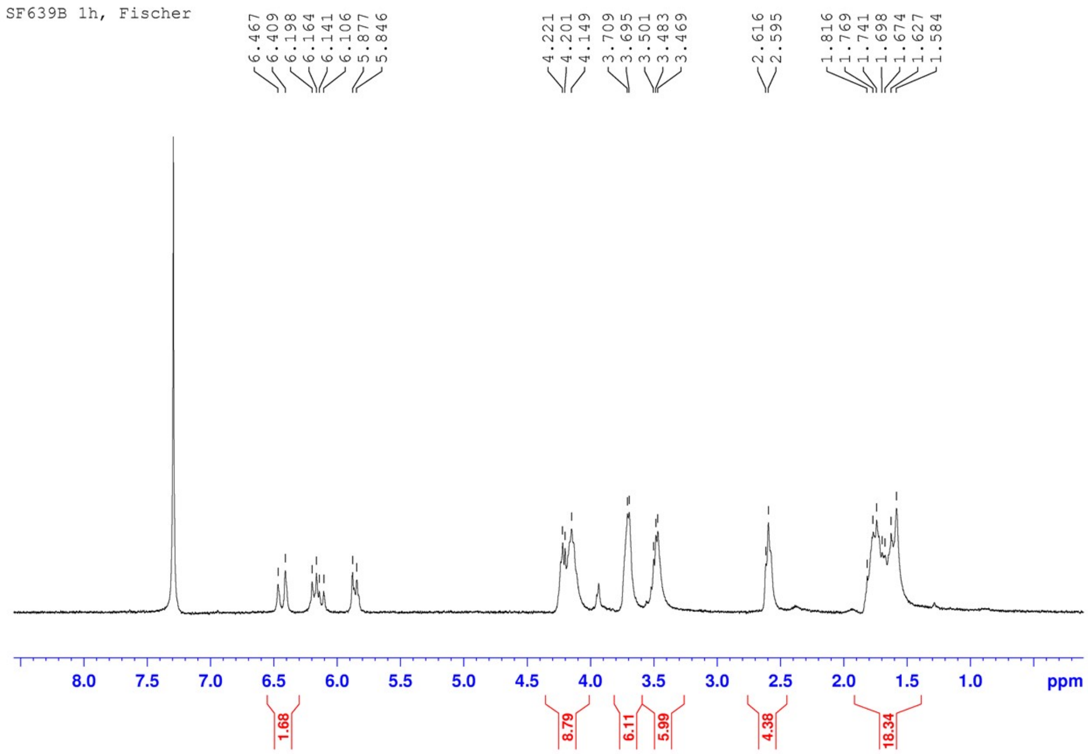


Figure S21 ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of the soluble part of reaction mixture of poly($BDDAcoBD_{0.5}$) after 18 h reaction time

4 BDDA as Michael acceptor for sequential polymerization

4.1 Two-stage curing

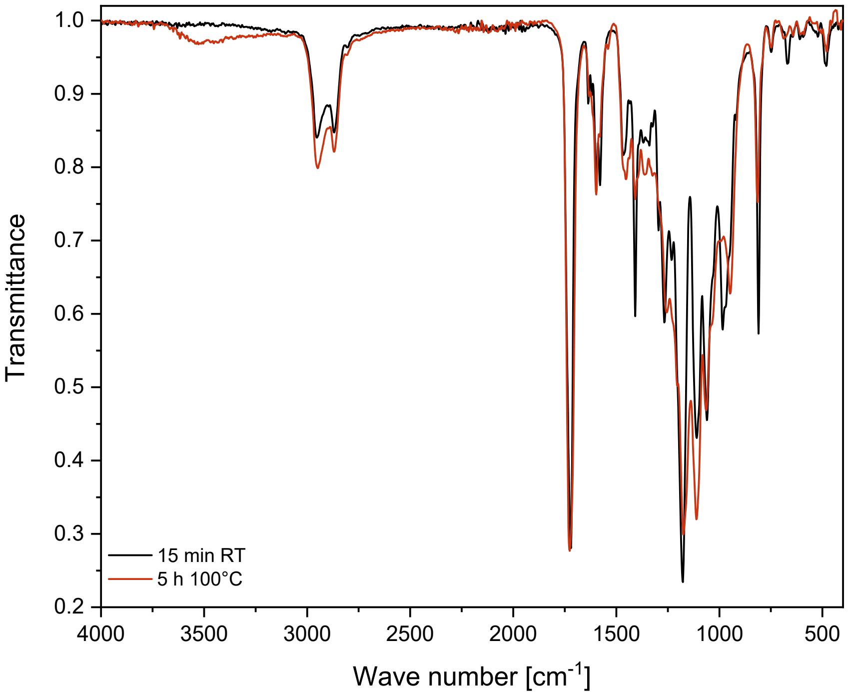


Figure S22 ATR-IR spectra of poly($BDDAcoBD_{0.5}$) after 15 min at room temperature (stage 1) and after 5 h at 100 °C (stage 2)

4.2 Determination of the extractable content

450.7 mg of poly(BDDAcoBD$_{0.5}$) was extracted at room temperature under stirring for 18 h with dichloromethane (10 mL). Afterwards, the solid residue was filtered off and washed. Dichloromethane was removed with an N_2 stream at 60 °C. Soluble fraction: 46.1 mg (10.3 wt%). The procedure was repeated with the solid residue and a second extraction was done as described above. Soluble fraction: 1.7 mg (0.4 wt%). The two extracts amount to 47.8 mg (10.6 wt%). From the ^{1}H NMR spectrum it could be identified that approximately 15 % of the soluble fraction consisted of TTMPP. However, the initiator (53.73 mg, 5 mol%) could not be fully recovered indicating that most of it is covalently bound to the polymer. Besides, the intensity of TTMPP oxidation products increased. No indications of TTMPP-DCM reaction products could be found.

Another extraction was done as described above but with acetone instead of dichloromethane. The two extracts amounted to 18.1 wt%. Dichloromethane and acetone extracts are similar.

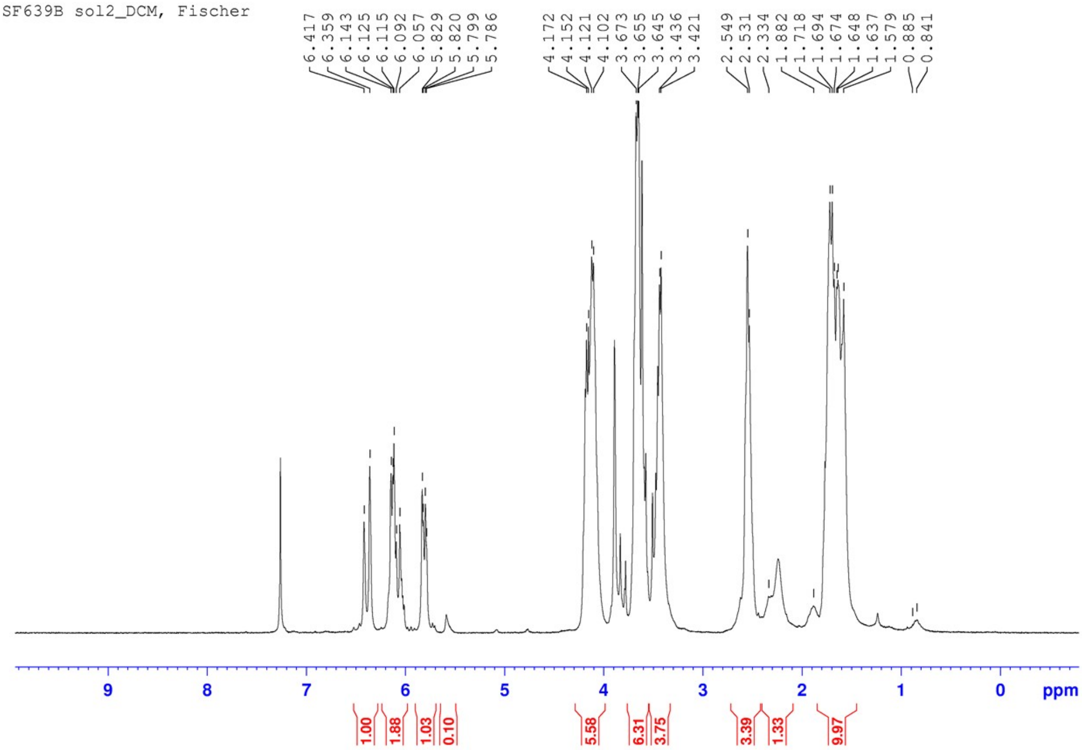


Figure S23 ^{1}H-NMR spectrum (300 MHz, $CDCl_3$) of the soluble fraction of poly(BDDAcoBD$_{0.5}$)

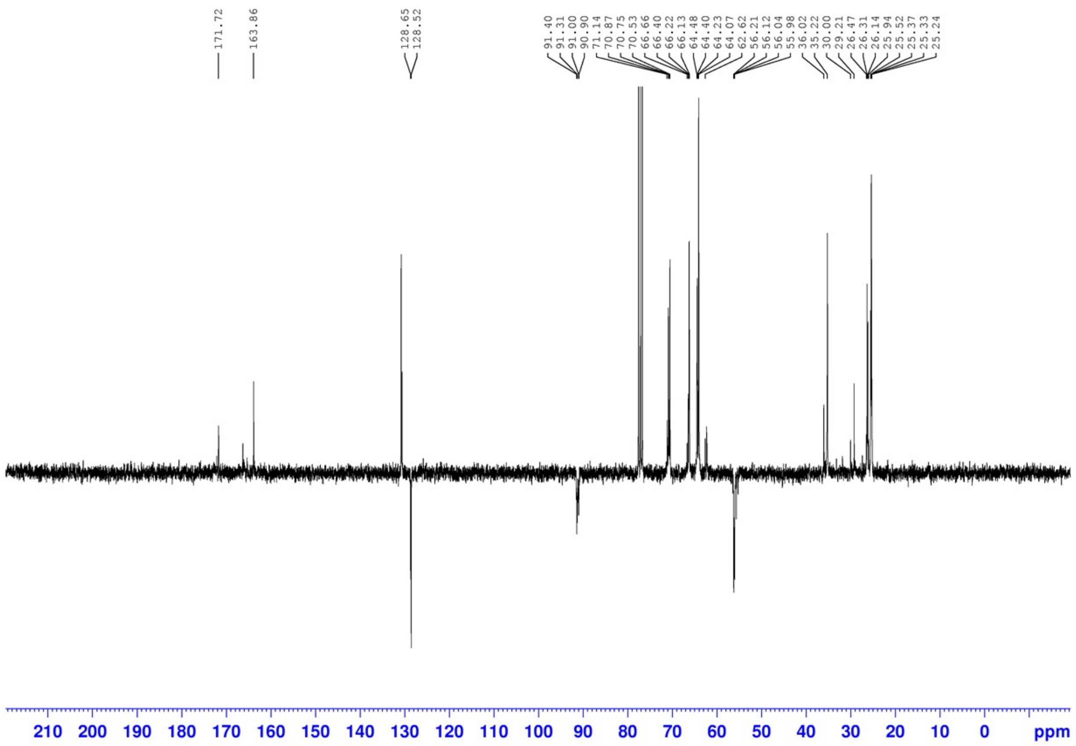


Figure S24 ^{13}C-APT spectrum (75.53 MHz, $CDCl_3$) of the soluble fraction of poly($BDDAcoBD_{0.5}$)

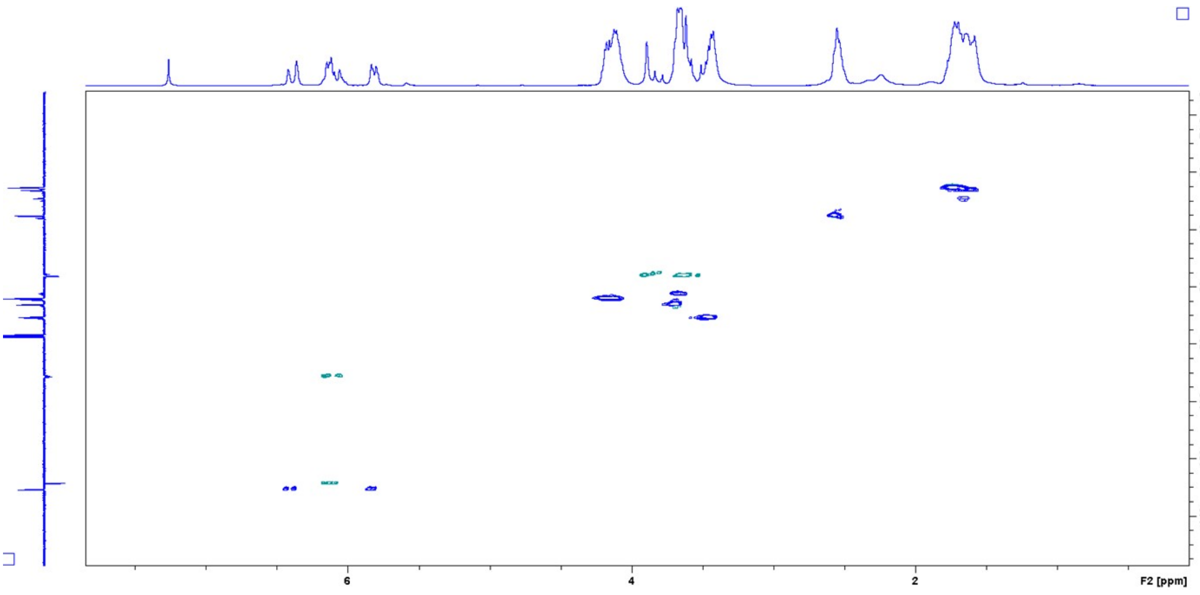


Figure S25 HSQC of the soluble fraction of poly($BDDAcoBD_{0.5}$)

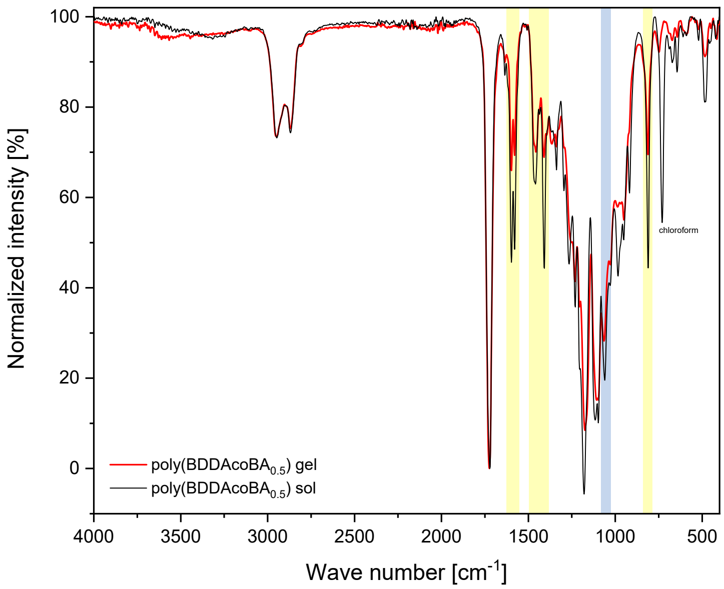


Figure S26 ATR-IR spectra of the solid (gel) and soluble (sol) fraction of poly(BDDAcoBD$_{0.5}$) and 5 mol% TTMPP at 60°C; yellow: representative bands of acrylate end groups; blue: representative ether band

4.3 Thermal analysis

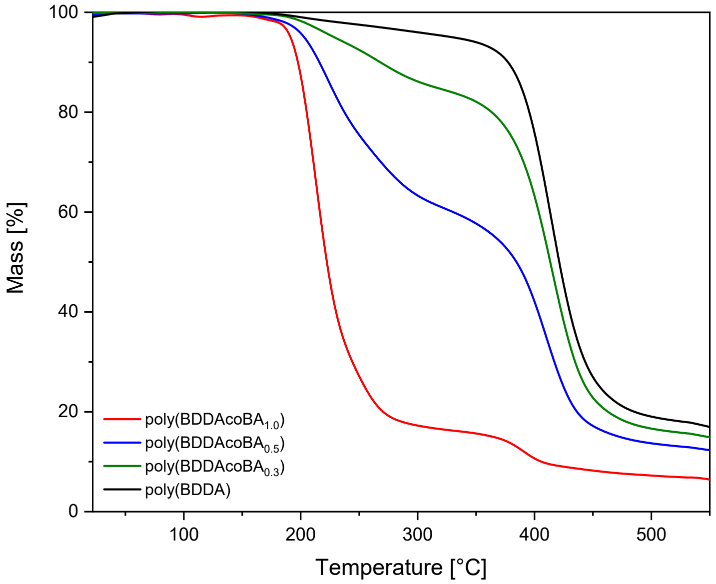


Figure S27 STA of poly(BDDAcoBD$_x$) with various ratios of butane-1,4-diol (BD)

Table S3 Glass transition temperatures (T_g) determined via DSC (40K/min) of polymers poly(BDDAcoBD$_x$) with different alcohol ratios

Alcohol equivalents	T_g [°C]
0.0	Not observed
0.2	+29°C
0.3	-22 °C
0.5	Not observed
1.0	Not observed

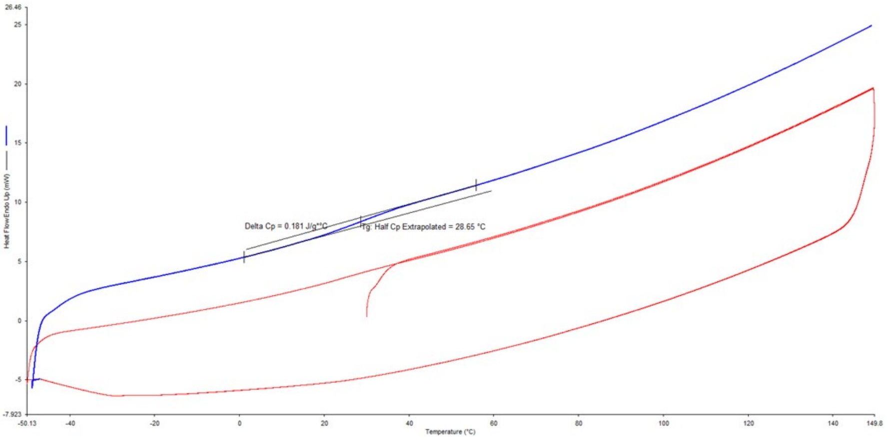


Figure S28 DSC measurement poly($BDDAcoBD_{0.3}$)

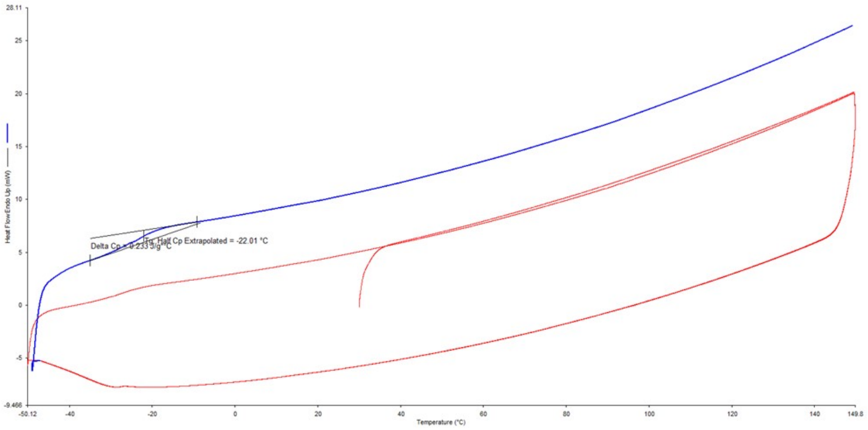


Figure S29 DSC measurement poly($BDDAcoBD_{0.2}$)

4.4 Size exclusion chromatography

The polymers synthesized with different amounts of butane-1,4-diol (poly(BDDAcoBA) were analyzed by size exclusion chromatography (Figure S30). Poly($BDDAcoBA_{1.0}$) already showed a small share of higher molar mass products after 15 min reaction time at room temperature. These products could also be observed by thermogravimetric analysis (cf. Figure S27). Accordingly, minor shares were also found for poly(BDDAcoBA0.5) after stage 1 curing (RT, 15 min). However, the molar mass and the viscosity of this sample is significantly lower compared to the stoichiometric one. After increasing the temperature to 100 °C for 1 h (stage 2 curing), the polymer could not be fully dissolved. The extract obtained from dichloromethane was subjected to SEC analysis and revealed the highest share of high molar mass species of all samples.

Table S4 Results of SEC analysis of BDDAcoBD polymers

Polymer	M_n [g/mol]	M_w [g/mol]	Đ
poly($BDDAcoBA_{1.0}$) RT 15 min	1000	1800	1.8
poly($BDDAcoBA_{0.5}$) RT 15 min	600	1000	1.7
poly($BDDAcoBA_{0.5}$) 100 °C 1 h	1200	4200	3.5

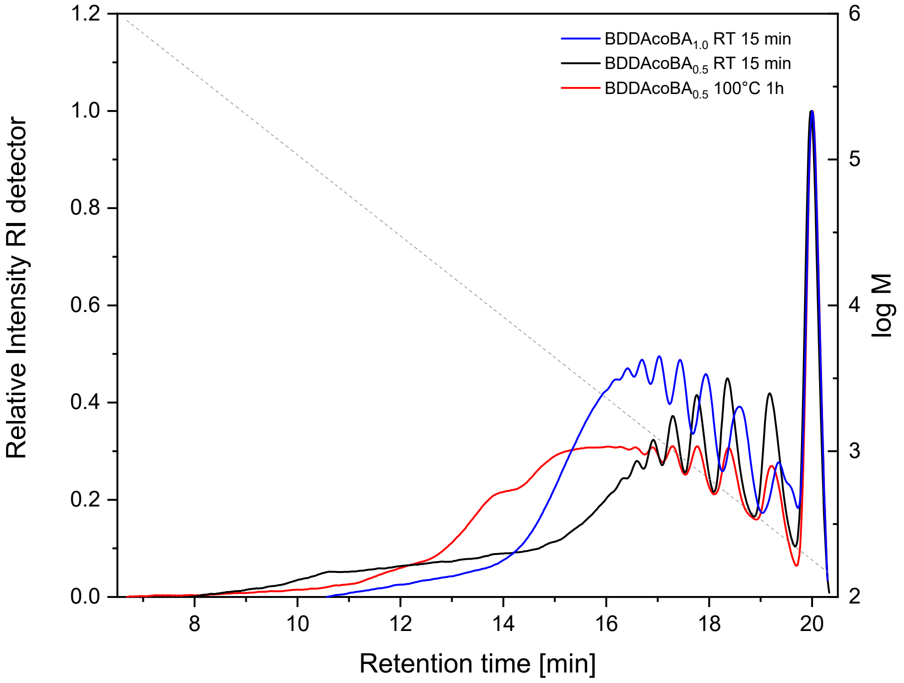


Figure S30 Size exclusion chromatograms (in THF, relative to poly(styrene) standards) of BDDAcoBA polymers

5 Divinyl sulfone as Michael acceptor for sequential polymerization

5.1 Two stage curing

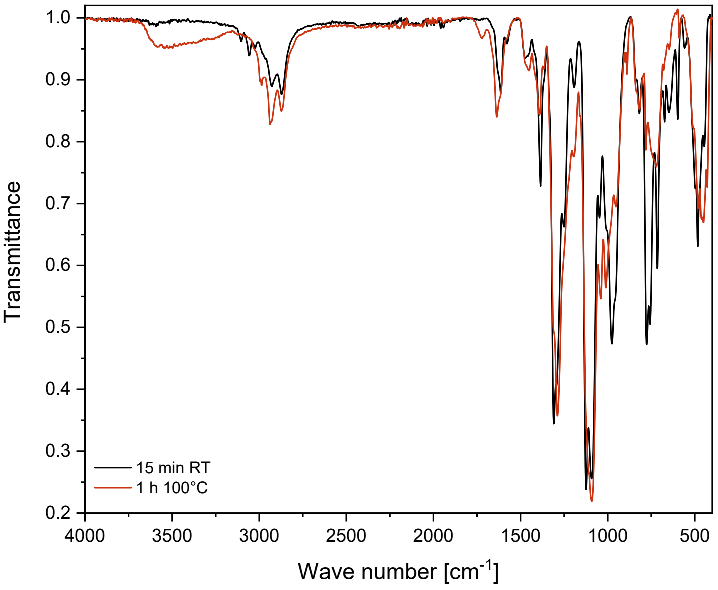


Figure S31 ATR-IR spectra of poly(DVScoBE$_{0.5}$) after 15 min at room temperature (stage 1) and after 1 h at 100°C (stage 2)

5.2 Reaction of divinyl sulfone with (Z)-butene-1,4-diol (poly(DVScoBE$_{0.5}$))

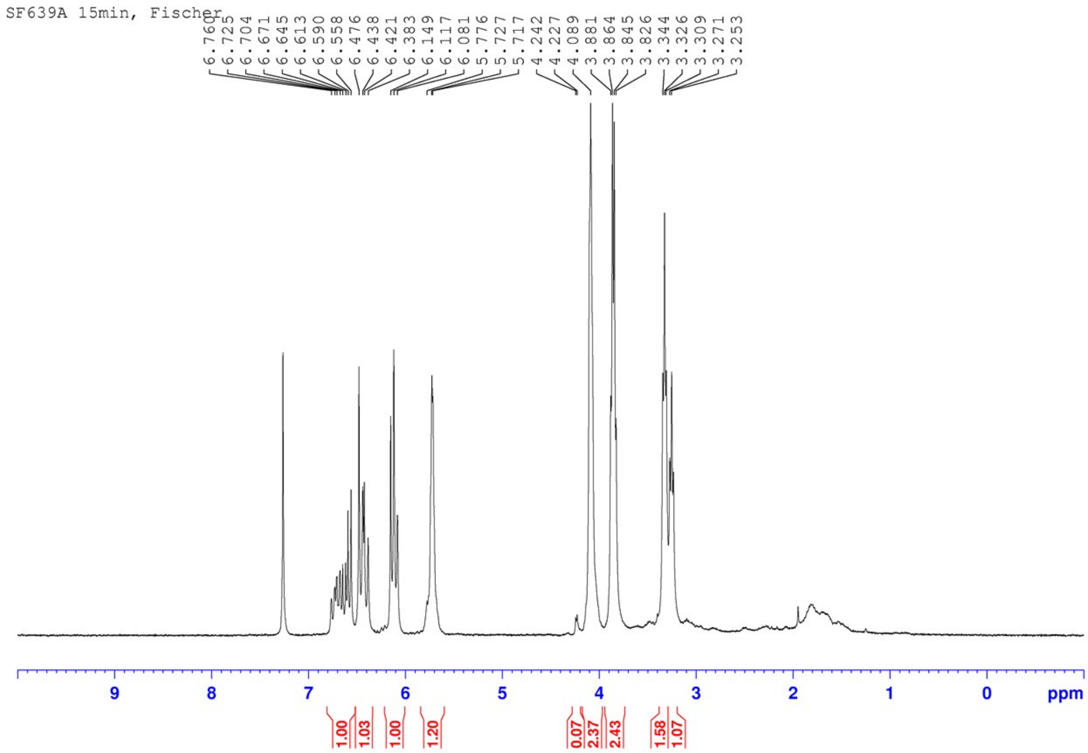


Figure S32 ^{1}H-NMR spectra (300 MHz, $CDCl_3$) of poly(DVScoBE$_{0.5}$) after 15 min at 60 °C with DBU (5 mol%) as catalyst

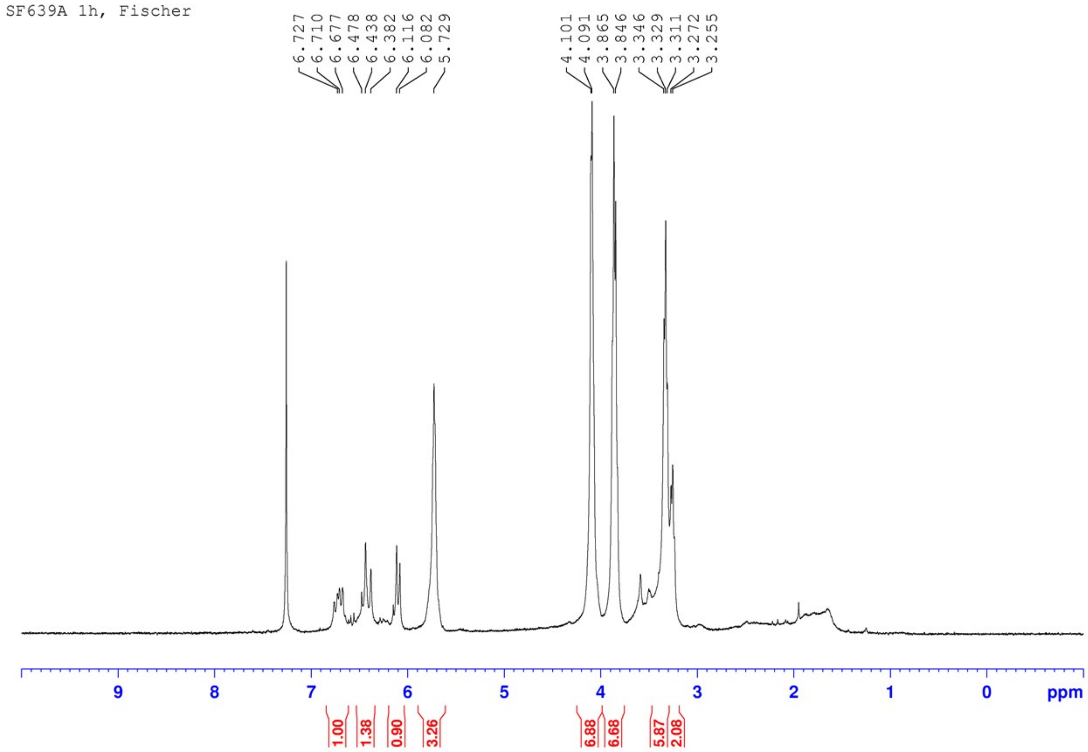


Figure S33 ^{1}H-NMR spectra (300 MHz, $CDCl_3$) of poly(DVScoBE$_{0.5}$) after 1 h at 60 °C with DBU (5 mol%) as catalyst

5.3 Determination of the extractable content

258.4 mg of poly(DVScoBE$_{0.5}$) was extracted at room temperature under stirring for 18 h with dichloromethane (5 mL). Afterwards, the solid residue was filtered off and washed. Dichloromethane was removed with an N_2 stream at 60°C. Soluble fraction: 31.8 mg (12.3 wt%). The procedure was repeated with the solid residue and a second extraction was done as described above. Soluble fraction: 12.1 mg (4.6 wt%). The two extracts amount to 43.9 mg (17.0 wt%).

Another extraction was done as described above but with acetone instead of dichloromethane. Crude polymer: 322.4 mg; First extract: 19.5 mg (6.0 wt%), second extract: 9.5 mg (3.0 wt%); Total: 29.0 mg (9.0 wt%). The same species could be detected in the dichloromethane and acetone extracts.

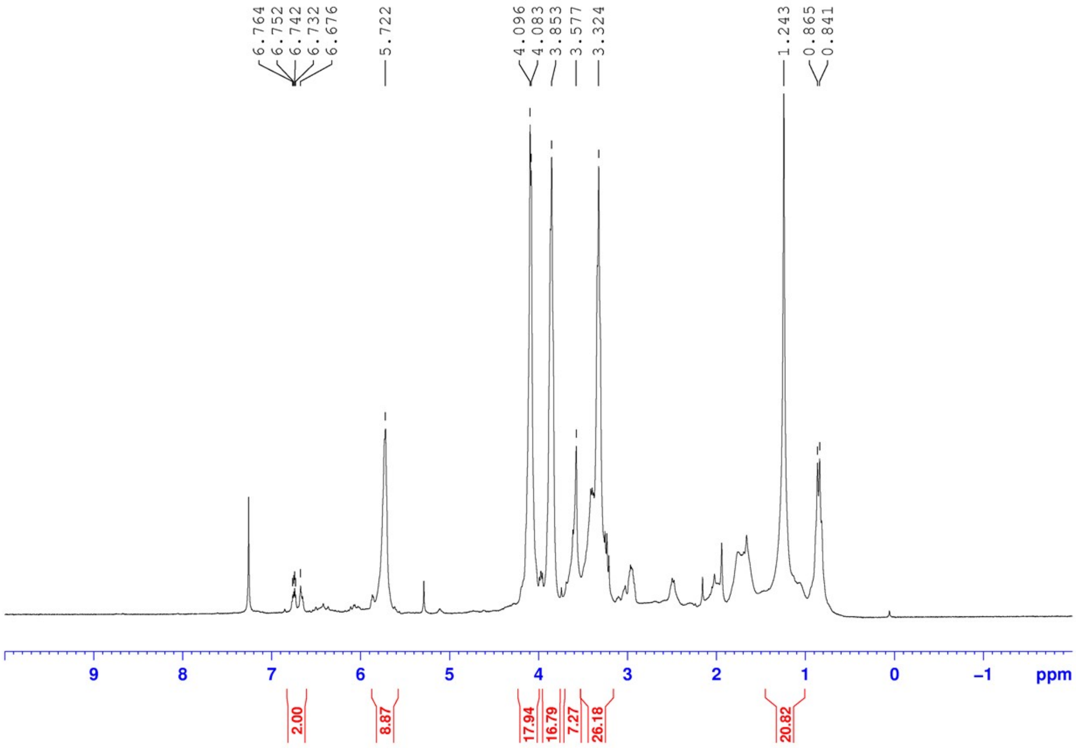


Figure S34 ^{1}H-NMR spectrum (300 MHz, $CDCl_3$) of the soluble fraction of poly(DVScoBE$_{0.5}$)

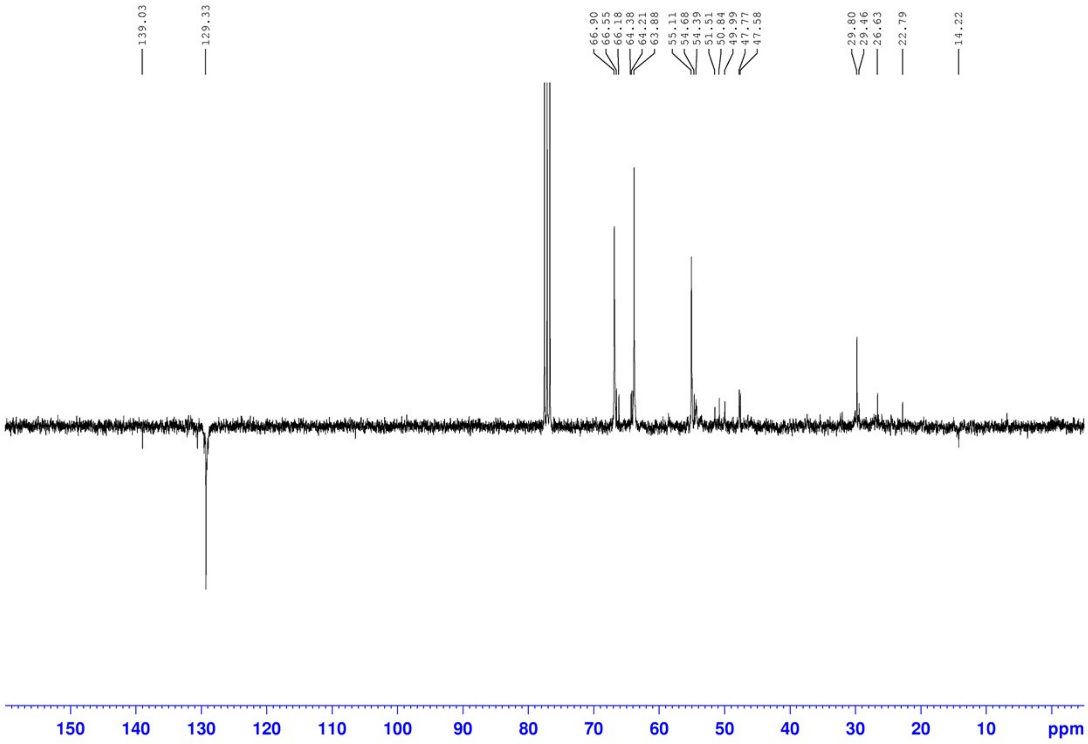


Figure S35 ^{13}*C-APT spectrum (75.53 MHz, CDCl*$_3$*) of the soluble fraction of poly(DVScoBE*$_{0.5}$*)*

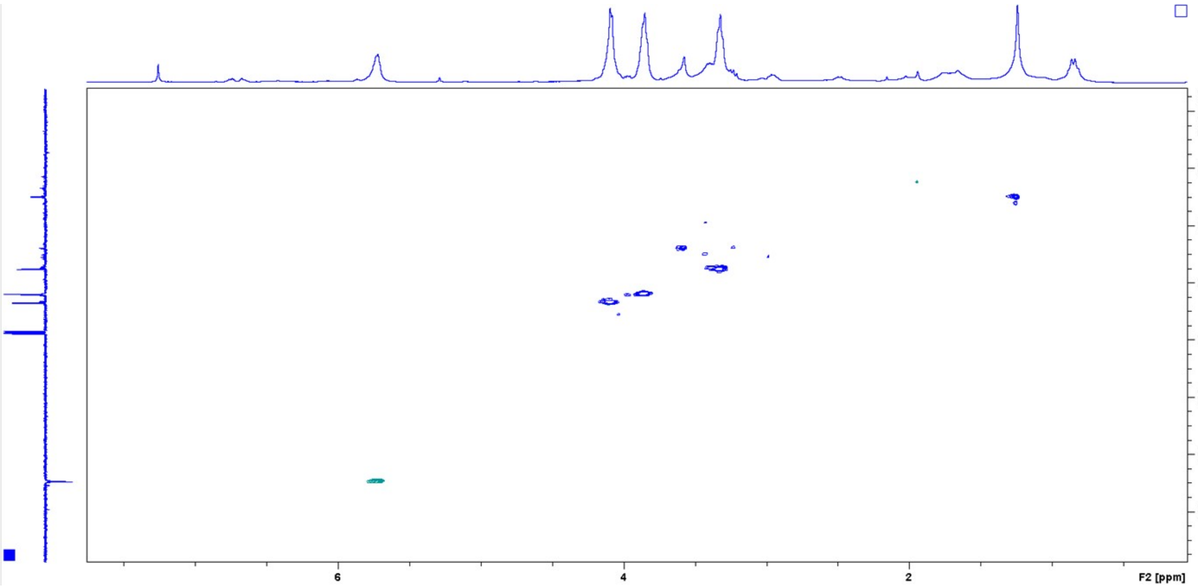


Figure S36 HSQC of the soluble fraction of poly(DVScoBE$_{0.5}$*)*

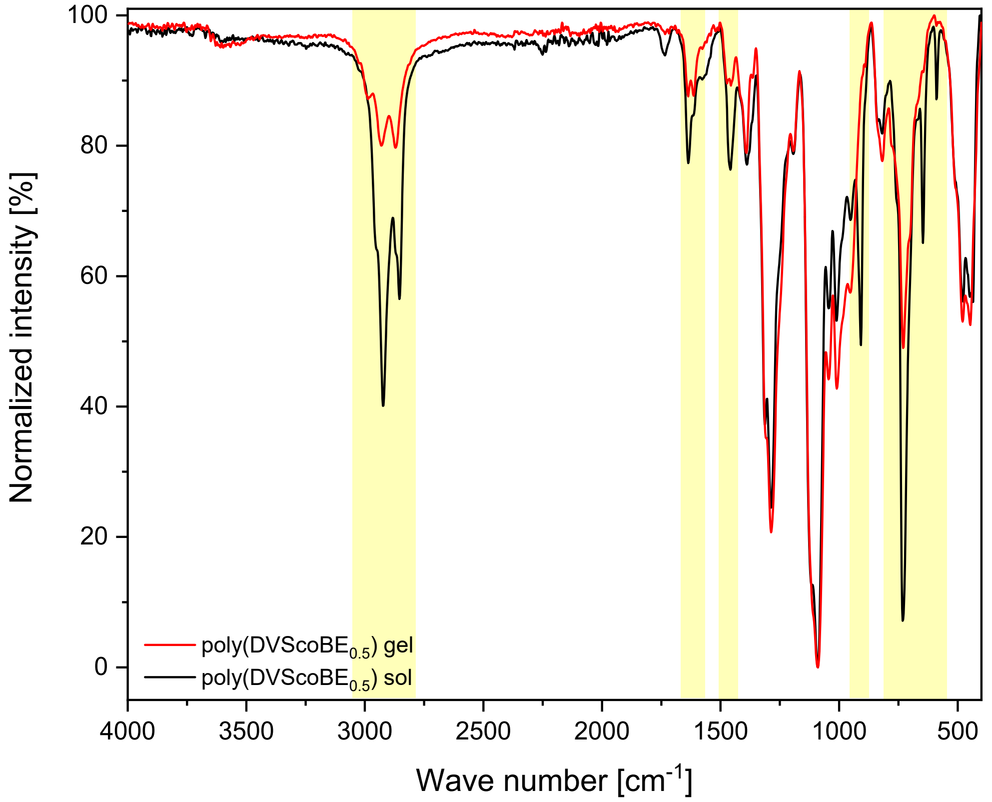


Figure S37 ATR-IR spectra of the solid (gel) and soluble (sol) fraction of poly(DVScoBE$_{0.5}$) and 5 mol% DBU at 60°C, deviations of intensities highlighted in yellow

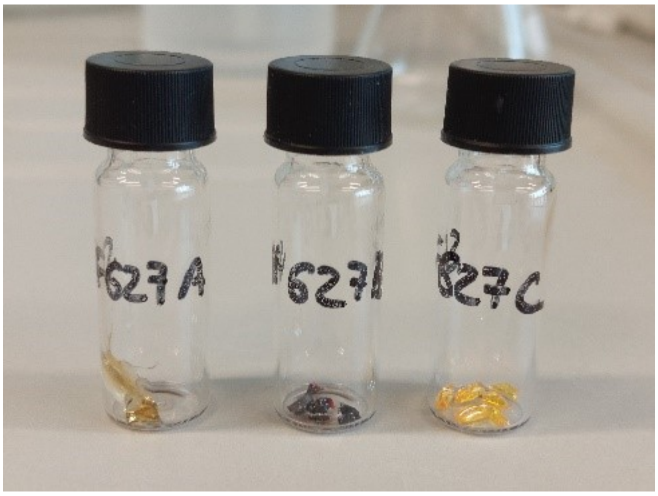


Figure S38 Obtained polymers of DVS and substochiometric amounts of alcohol after 24 h at 60°C; left: poly(DVScoBE$_1$), middle: poly(DVScoBE$_{0.5}$), right: 0 equiv. alcohol (polyDVS)

5.4 Thermal analysis

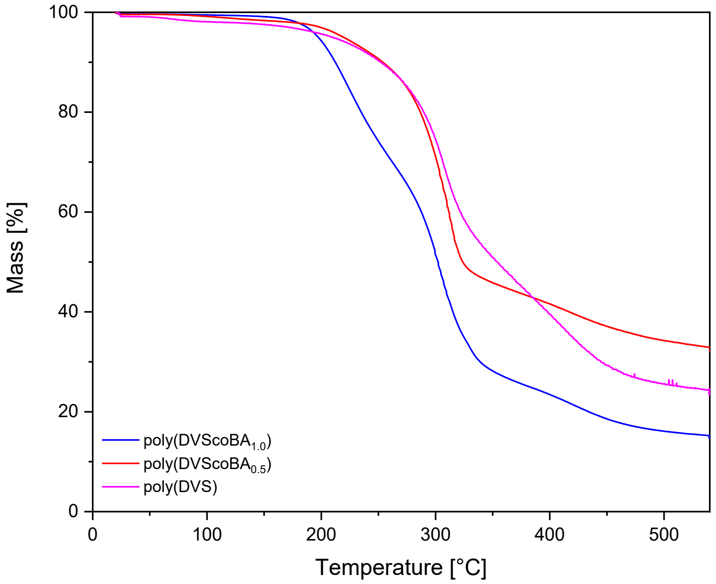


Figure S39 TG analyses of poly(DVScoBA$_x$) x = 1, 0.5, 0

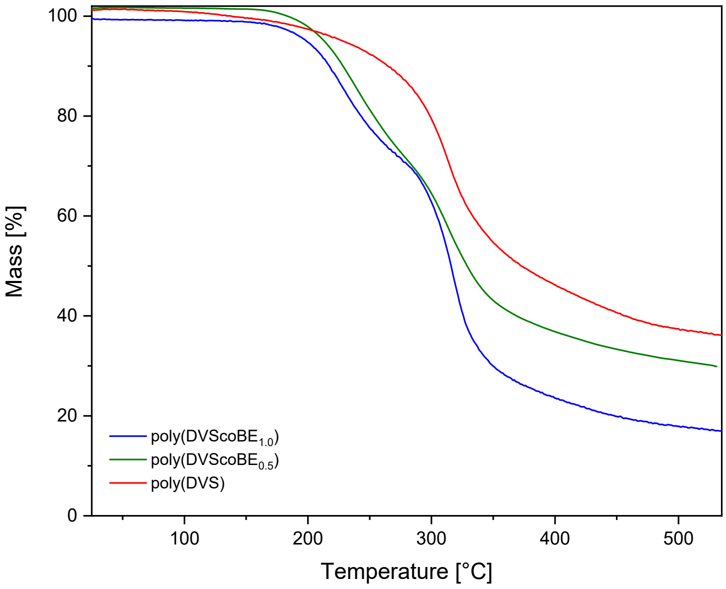


Figure S40 TG analyses of poly(DVScoBE$_x$) x = 1, 0.5, 0

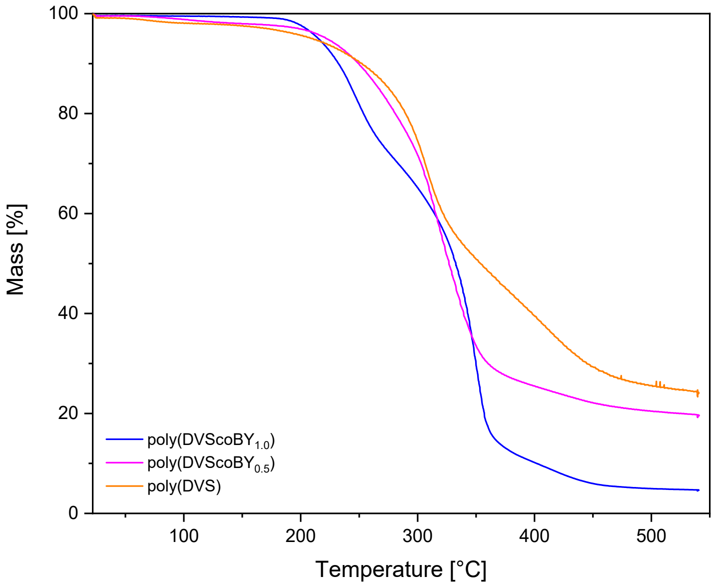


Figure S41 TG analyses of poly(DVScoBY$_x$) x = 1, 0.5, 0

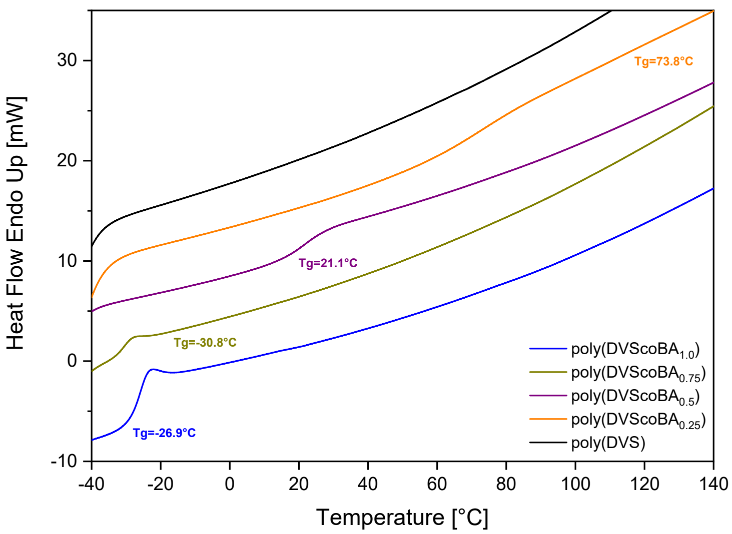


Figure S42 DSC measurements of poly(DVScoBA$_x$) x = 1, 0.75, 0.5, 0.25, 0 – 3rd heating run: 40 °C/min

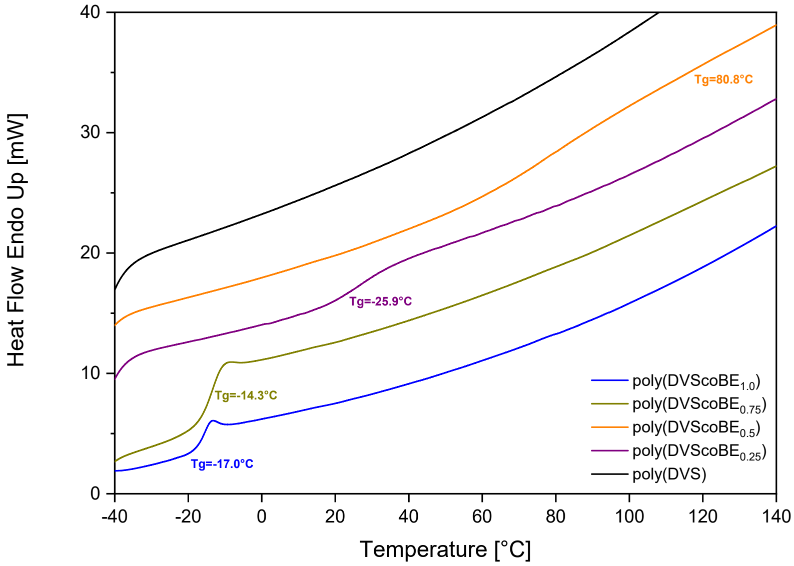


Figure S43 DSC measurements of poly(DVScoBE$_x$) x = 1, 0.75, 0.5, 0.25, 0 – 3rd heating run: 40 °C/min

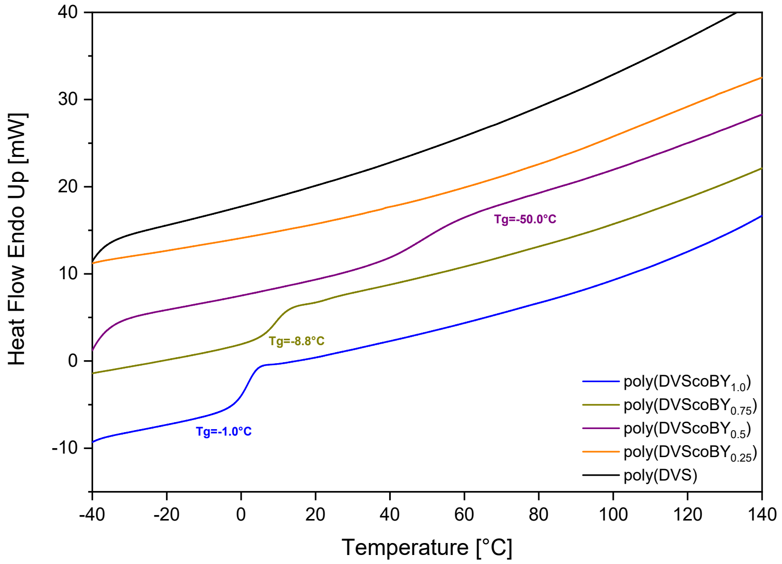


Figure S44 DSC measurements of poly(DVScoBY$_x$) x = 1, 0.75, 0.5, 0.25, 0 – 3rd heating run: 40 °C/min

6 Self-Healing

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 (130 °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.

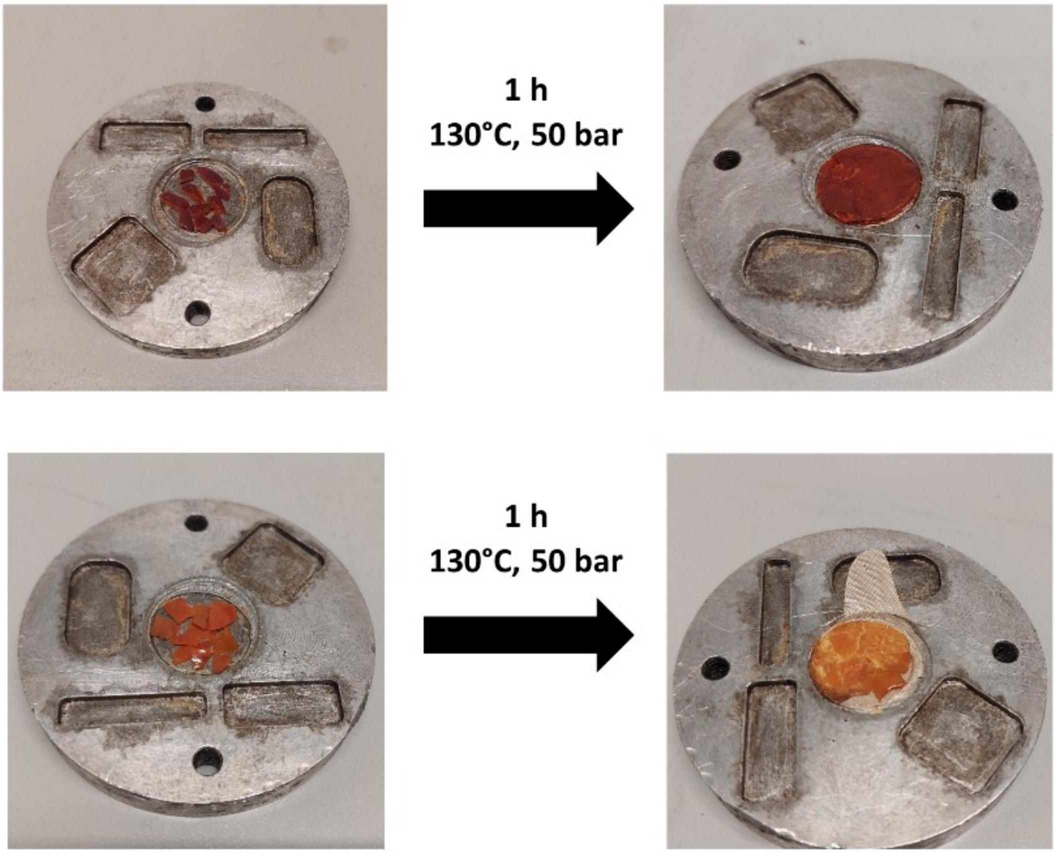


Figure S45 Self-healing of poly(DVScoBE$_{0.5}$) (top) and unsuccessful self-healing of poly(DVScoBE$_{0.25}$) (bottom)

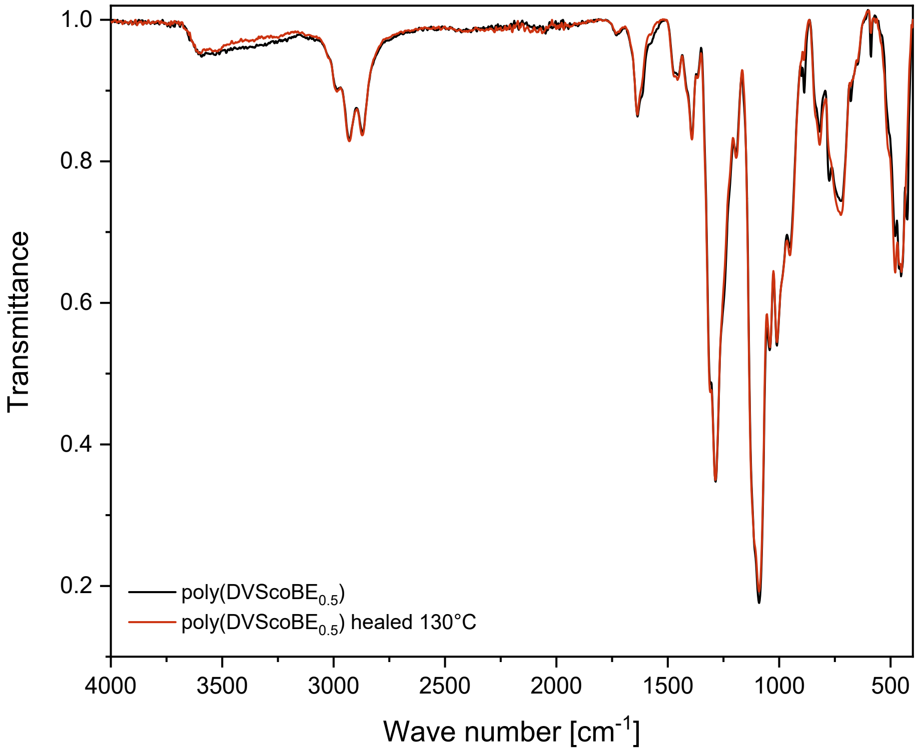
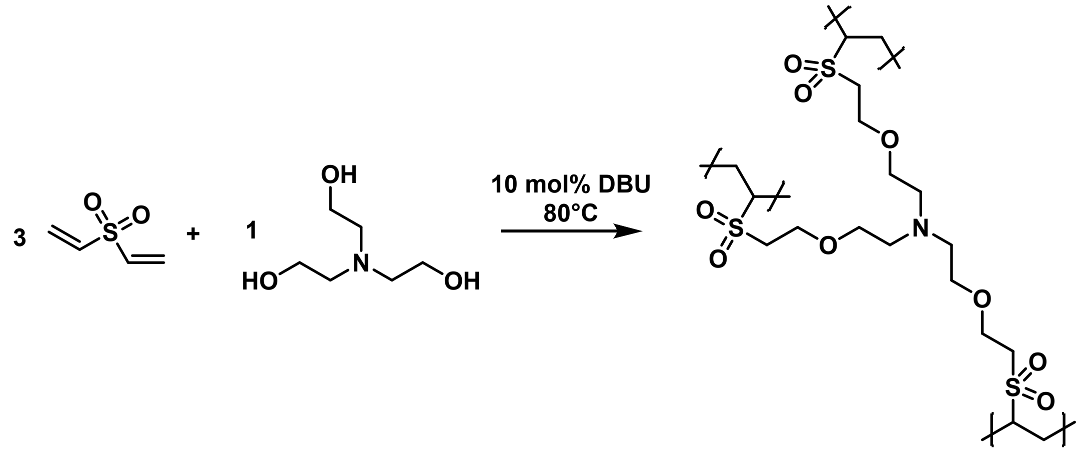


Figure S46 ATR-IR spectra of poly(DVScoBE$_{0.5}$) and the reprocessed polymer

6.1 Synthesis and reprocessing of poly(DVScoTEA$_{0.33}$)

A 4 mL reaction vessel was charged with 1.00 g (8.40 mmol, 3.00 equiv.) divinyl sulfone and half of the necessary amount of triethanolamine (8.40 mmol, 0.42 g, 1.00 equiv.). The other half of triethanolamine was mixed with 10 mol% DBU (125 µL, 0.84 mmol, 0.30 equiv.). The alcohol-DBU mixture was then added to the divinyl sulfone-alcohol mixture and stirred for about 2 min 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 1 h to avoid post-curing in the hot press.



Scheme S2 Synthesis of poly(DVScoTEA$_{0.33}$)

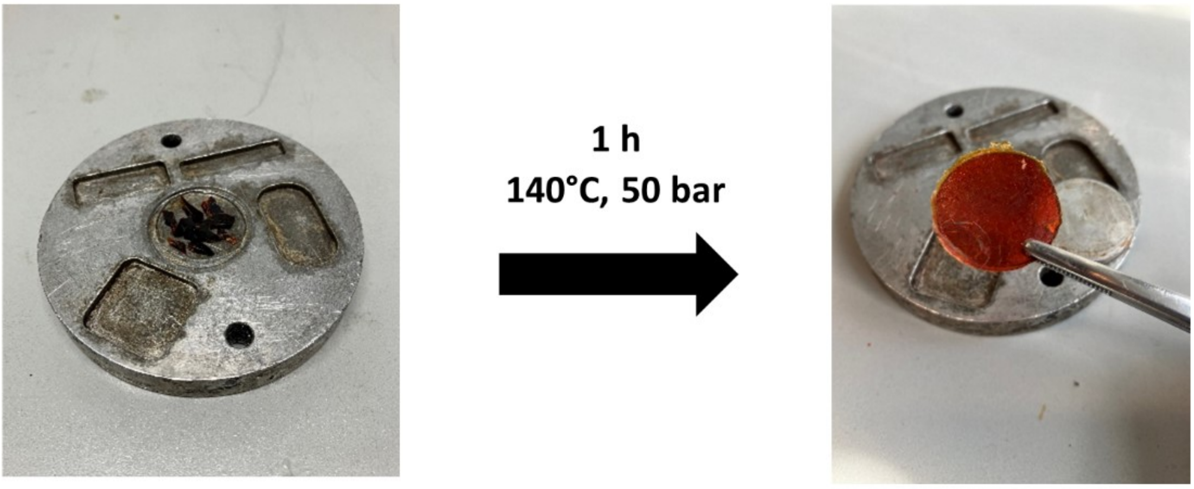


Figure S47 Self-healing of poly(DVScoTEA$_{0.33}$)

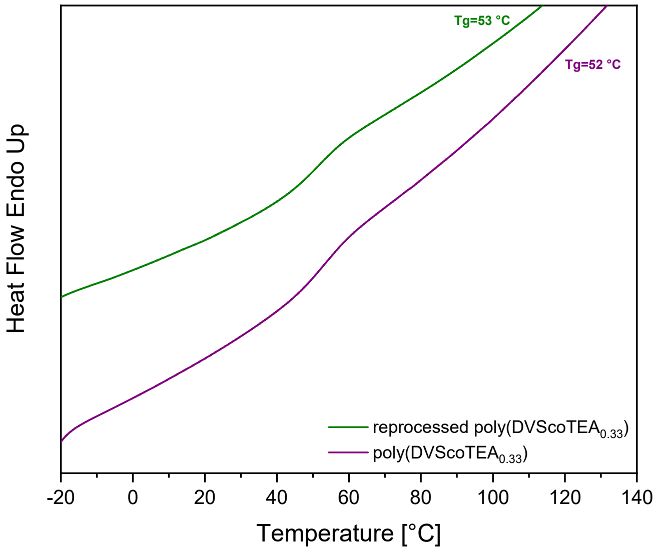


Figure S48 DSC curves of 3rd heat run (heating rate of 40°C/min) of poly(DVScoTEA$_{0.33}$) after post-curing and after hot press experiment at 140°C