Electronic Supplementary Material (ESI) for Polymer Chemistry

Supporting Information

One-pot, Additive-free Preparation of Functionalized Polyurethanes via Amine-thiol-ene Conjugation

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Methods

^{1}H- and ^{13}C-NMR (Attached Proton Test, APT) spectra were recorded in $CDCl_3$ on a Bruker AM500 spectrometer at 500 MHz or on a Bruker Avance 300 at 300 MHz. Chemical shifts are presented in parts per million (δ) relative to $CHCl_3$ (7.26 ppm in ^{1}H- and 77.23 ppm in ^{13}C-NMR respectively) or DMSO-d_6 (2.50 ppm in ^{1}H- and 39.51 ppm in ^{13}C-NMR respectively) as internal standard. Coupling constants (*J*) in ^{1}H-NMR are given in Hz. The resonance multiplicities are described as *d* (doublet) or *m* (multiplet). An Agilent technologies 1100 series LC/MSD system equipped with a diode array detector and single quad MS detector (VL) with an electrospray source (ESI-MS) was used for classic reversed phase LC-MS (liquid chromatography mass spectroscopy) and MS analysis. Analytic reversed phase HPLC was performed with a Phenomenex C_{18} (2) column (5 µ, 250 x 4.6 mm) using a solvent gradient (0 → 100% acetonitrile in H_2O in 15 min) and the eluting compounds were detected *via* UV-detection (λ = 214 nm). High resolution mass spectra (HRMS) were collected using an Agilent 6220 Accurate-Mass time-of-flight (TOF) equipped with a multimode ionization (MMI) source. Time-resolved online ATR FT-IR spectra were recorded on a React-IR 4000 Instrument (Mettler Toledo AutoChem ReactIR) equipped with a silicon ATR probe (SiComp, optical range 4400–650 cm^{-1}). For *online* monitoring, the silicon probe was introduced into a two-necked glass flask containing the reaction mixture and spectra were recorded every minute. The solvent spectrum was recorded at the reaction temperature and subtracted to enhance the signal of the reaction species. Curve-fittings of FT-IR spectra were performed using Bruker OPUS software (version 4.2). The parameters were optimized using a Levenberg–Marquardt algorithm.[1] FT-ATR-IR spectra were recorded on a Perkin-Elmer Spectrum1000 FTIR infrared spectrometer with pike-HATR module. GC-FID analyses were performed using a Hewlett Packard 5890 series II equipped with a Restek XTI-5 capillary column (30 mm x 0.25 mm, 0.25 µm film thickness of 5 % diphenyl and 95 % PDMS). The carrier gas (H_2) was used at a flow rate of 1.4 mL/min. After sample injection, the column oven was kept at 50 °C for 3 min, then heated until 240 °C at a rate of 20 °C/min and finally kept at 240 °C for 5 min. Size Exclusion Chromatography (SEC) was performed using two different systems: (i) a Waters instrument, with a refractive-index (RI) detector (2414 Waters), equipped with 3 Polymer Standards Services GPC serial columns (1 X GRAM Analytical 30 Å, 10 µm and 2 x GRAM Analytical 1000 Å, 10 µm) at

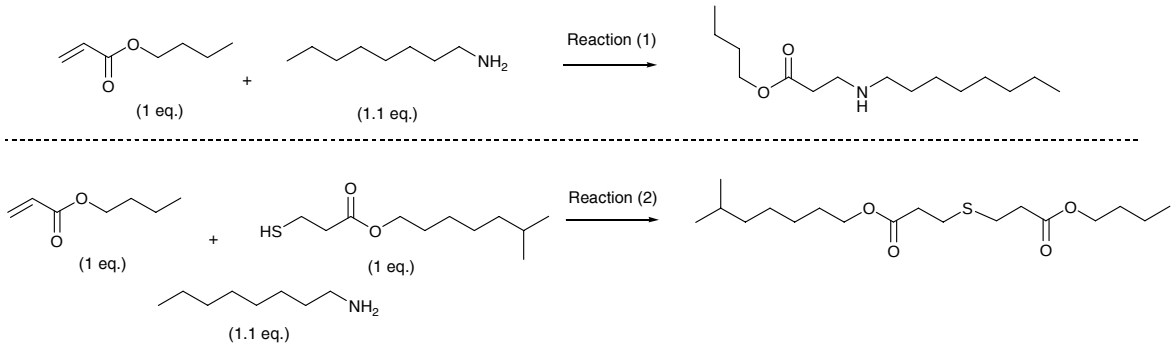
35 °C. Poly(methyl methacrylate) (PMMA) standards were used for calibration and *N,N*-dimethylacetamide (DMA), containing LiBr (0.42 g/mL) was used as a solvent at a flow rate of 1 mL/min. Molar mass and dispersity were determined using the Empower software; (ii) a Varian PLGPC50plus instrument, using a refractive index detector, equipped with two Plgel 5 µm MIXED-D columns 40 °C. Polystyrene standards were used for calibration and THF as eluent at a flow rate of 1 mL/min. Samples were injected using a PL AS RT autosampler. The preparative SEC setup consists of a Shimadzu LC-2OAT pump, a Shimadzu SIL-IOAF autosampler, a RID-IOA Differential Refractive Index Detector, a FRC-1OA Fraction Collector, CBM-2OA PC Interface/System Controller. Columns are from Shodex: a K-LG guard column and a KF-2004 prep column (elution 2.5 mL/min, THF, rt). MALDI-TOF (Matrix-Assisted Laser Desorption and Ionization Time of Flight) mass spectrometry analysis was performed on an Applied Biosystems Voyager-DE STR instrument equipped with nitrogen laser operating at 337 nm, pulsed ion extraction source and reflectron detector. The laser pulse width is 3 ns and maximum power is 20 Hz. Spectra were recorded in the linear mode with an acceleration voltage of 19 kV and delay of 100 ns. 100 single shot acquisitions were summed to give the spectra and the data were analyzed using Data Explorer and Polymerix software.

Samples were prepared by dissolving the matrix dithranol in the solvent (THF, 20 mg/mL), mixing with the polymer (1 mg/mL) and potassium trifluoroacetate in acetone (15 mg/mL) that has been used as cationizing agent. Thermogravimetric analysis (TGA) was performed with a Mettler Toledo TGA/SDTA851e instrument under air atmosphere at a heating rate of 10 °C/min from 25 to 800 °C. All curves are blank corrected (run with an empty pan under the same conditions).

Materials

1,4-Cyclohexanedimethanol monoacrylate ([23117-36-4], 95 %) was kindly provided by Nippon Kasei. Glycine t-butylester ([6456-74-2], 97 %) and Pyridine ([110-86-1], 99.5 %) were purchased from Alfa Aesar. Chloroform D ([865-49-6], ≥ 99.8 %) and DMSO-d_6 ([2206-27-1], ≥ 99.8 %) were purchased from Euriso-top. Jeffamine® M-600 was purchased from Huntsmann. DL-Homocysteinethiolactone hydrochloride ([6038-19-3], 99 %) and Triethylamine ([121-44-8], 99 %) were purchased from Acros Organics. Allylamine ([107-11-9], ≥ 99 %), Benzylamine ([100-46-9], ≥ 99.5 %), *n*-Butyl acrylate ([141-32-2], ≥ 99 %), Chloroform ([865-49-6], ≥ 99.8 %), Dichloromethane ([75-09-2], ≥ 99.8 %), *N,N*-Dimethylethylenediamine ([108-00-9], ≥ 98 %), Dodecane ([112-40-3], ≥ 99 %), Furfurylamine ([617-89-0], ≥ 99 %), Diethylether ([60-29-7], ≥ 99.9 %), 2-Hydroxyethylacrylate ([818-61-1], 96 %), Isooctyl 3-mercaptopropionate (IoMP, [30374-01-7], ≥ 99 %), *N*-Methylmaleimide ([930-88-1], ≥ 99.0 %), 3-Morpholinopropylamine ([123-00-2], > 98 %), 1-Octanethiol ([111-88-6], ≥ 98.5 %), *n*-Octylamine ([111-86-4], 99 %), Pentaerythritol tetrakis(3-mercaptopropionate) ([7575-23-7], > 95 %), Phosgene ([75-44-5], ~ 20 % solution in toluene), Propargylamine ([2450-71-7], 98 %), *n*-Propylamine ([107-10-8], ≥ 99 %), Tetrahydrofuran ([109-99-9], ≥ 99 %) and γ-Thiobutyrolactone ([1003-10-7], 98 %) were purchased from Sigma-Aldrich and used without purification. Solvents (CH_2Cl_2 and pyridine) for the monomer synthesis were distilled from CaH_2 prior to use. Silicagel (ROCC, SI 1721, 60 Å, 40 – 63 µm) was used to perform preparative column chromatography, eluting with technical solvents. The collected fractions were analyzed by thin layer chromatography (TLC-plates, Macherey-Nagel, SIL G-25 UV_{254}).

Model studies and kinetics



Scheme S 1 - Aza-Michael addition *vs* thiol-Michael addition. Two model reactions were performed for FT-IR *online* monitoring of the reaction progress. Reaction (1) is comprised of 1 eq. of *n*-butyl acrylate and 1.1 eq. of *n*-octylamine. Reaction (2) is comprised of 1 eq. of *n*-butyl acrylate, 1 eq. of IoMP and 1.1 eq. of *n*-octylamine.

Acrylate and thiol conversions were *online* monitored by decreases in FT-IR absorption intensity of the acrylate double bond wagging vibrations (987-968 cm^{-1}) and thiol SH stretching (2582 cm^{-1}), respectively (Figure S 1). The solvent spectrum was subtracted to enhance the signal of the reaction species. The conversion of the acrylate double bond was additionally confirmed by decreases in absorption intensity of the other acrylate $CH=CH_2$ vibrations, such as the twisting, scissoring and stretching ones at 814, 1409, 1638 and 1622 cm^{-1}, respectively, as well as shifts of the C=O ester stretching signal – originating from the ester signals of both *n*-butyl acrylate and IoMP – to a slightly higher wavenumber ascribed to the ester groups in the formed products. During the reaction, the intensity of the C-H stretches (3000-2850 cm^{-1}) was constant, indicating that there was no change in intensity of the other bands due to solvent evaporation.

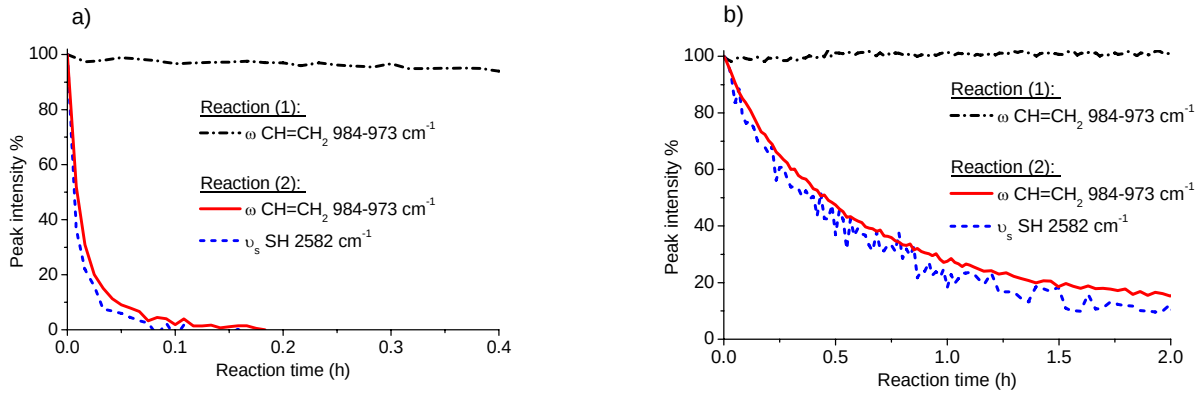
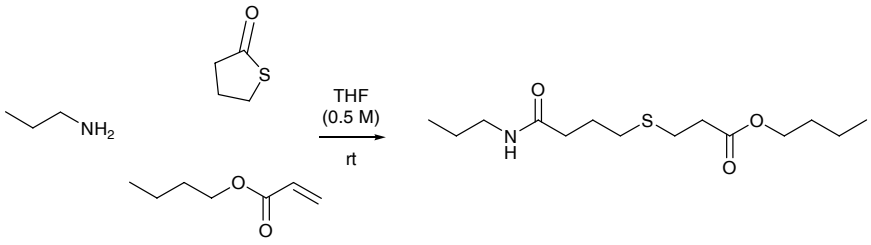


Figure S 1 - Aza-Michael addition *vs* Thiol-Michael addition. Two model reactions (Scheme S 1) were performed in different solvents and concentrations: a) at a *n*-butyl acrylate concentration of 1 M in THF and b) at a *n*-butyl acrylate concentration of 0.5 M in $CHCl_3$. Peak intensities of thiol and/or acrylate as a function of time reflect the kinetic profiles.



Scheme S 2 - Model amine-thiol-ene conjugation between *n*-propylamine, γ-thiobutyrolactone and *n*-butylacrylate.

With the use of 1.1 eq. of *n*-propylamine, the reaction was not complete after 9 hours of measurement. Thus, in order to deconvolute the FT-IR spectra, 2 eq. of *n*-propylamine was used to speed up the reaction. Therewith, the reaction was complete after 8 h. FT-IR spectra of the reactants (Scheme S 2) and corresponding spectral assignments can be seen in Figure S 2 and Table S 1. A comparison of FT-IR spectra, with assigned characteristic vibrational bands, recorded for the reaction at different reaction times, is shown in Figure S 3.

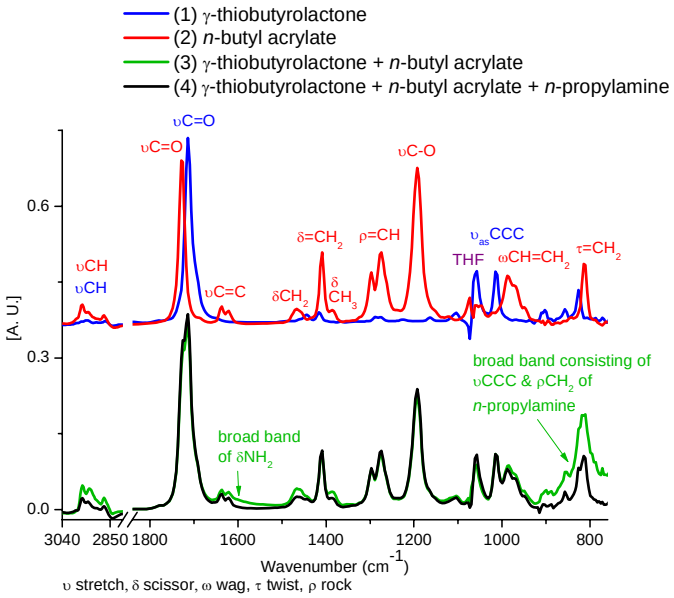


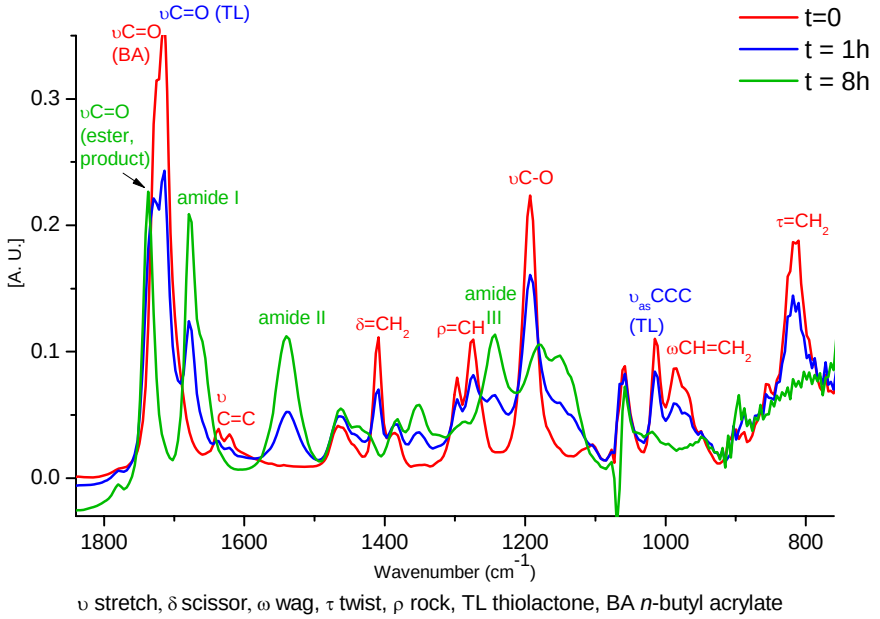
Figure S 2 - FT-IR spectra recorded for the reaction of butyl acrylate (1 eq.) with γ-thiobutyrolactone (1 eq.) in the presence of *n*-propylamine (2 eq.), at an acrylate concentration of 0.5 M in THF, at room temperature and under air condition: (3) prior to addition of *n*-propylamine, (4) right after addition of *n*-propylamine. For comparison, separate spectra of (1) γ-thiobutyrolactone and (2) *n*-butyl acrylate were recorded in the same solvent.

Table S 1 - Selected observed vibrational frequencies (cm^{-1}) and spectral assignments for the reaction of *n*-butyl acrylate with γ-thiobutyrolactone in THF in the presence of *n*-propylamine.

n-butyl acrylate		γ-thiobutyrolactone	
Wavenumber (cm^{-1})	Assignment[a]	Wavenumber (cm^{-1})	Assignment[a]
1728	ν(C=O)	1718	ν(C=O)
1638, 1622	ν(C=C)	1451	$\delta(CH_2)$
1467	$\delta(CH_2)$	1420	$\delta(CH_2)$
1409	$\delta(=CH_2)$	1294, 1278	$\omega(CH_2)$
1386	$\delta(CH_3)$	1224	$\tau(CH_2)$
1297, 1278	ρ(=CH)	1165	$\tau(CH_2)$
1190	ν(C-O)	1106	$\tau(CH_2)$
987, 968	$\omega(CH=CH_2)$	1015	$\nu_{as}(C_4\text{-}C_3\text{-}C_2)$
814	$\tau(=CH_2)$	911	$\nu_{s}(C_4\text{-}C_3\text{-}C_2)$
		861, 826	$\rho(CH_2)$
n-propylamine		formed product	
Wavenumber (cm^{-1})	Assignment[a]	Wavenumber (cm^{-1})	Assignment[a]
1610	NH_2 symmetric deformation	1737	ν(C=O) (ester)
1463	CH_2 deformation	1678	amide I (νC=O, νC-N)
1390	CH_3 deformation	1540	amide II (δN-H, νC-N)
890-700	CCC stretch, CH_2 rock, NH_2 wag	1244	amide III

ν stretch, δ scissor, ω wag, τ twist, ρ rock

[a] Assignments from reported vibrational studies[2-7] were compared to assign the bands observed in the experimental spectra.



υ stretch, δ scissor, ω wag, τ twist, ρ rock, TL thiolactone, BA *n*-butyl acrylate

Figure S 3 - FT-IR spectra as a function of reaction time recorded for the model reaction of butyl acrylate (1 eq.) with γ-thiobutyrolactone (1 eq.) in the presence of 2 eq. of *n*-propylamine, at an acrylate concentration of 0.5 M in THF, at room temperature and under air atmosphere.

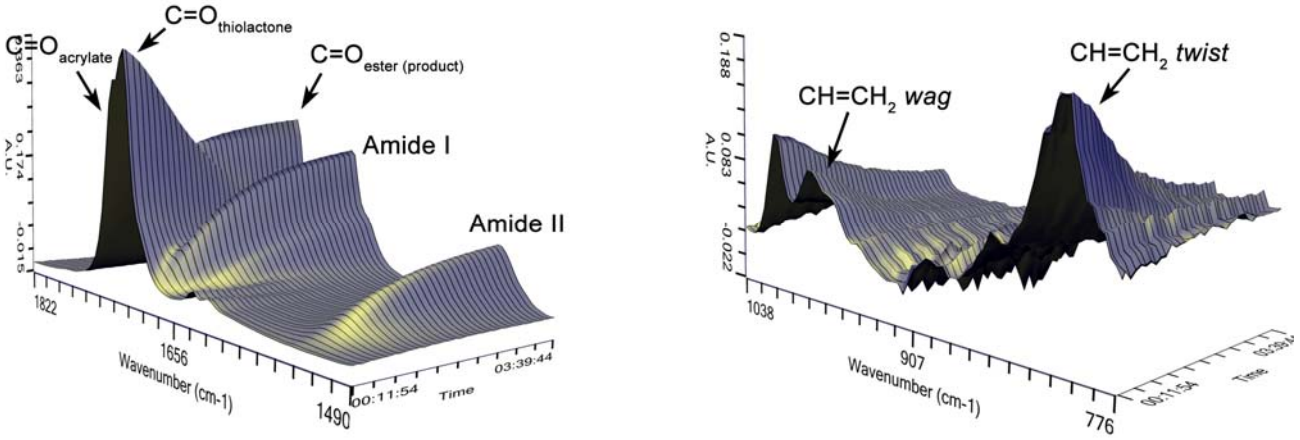


Figure S 4 - *Online* FT-IR waterfall plots of relevant vibrational bands demonstrating the progress of the model reaction of butyl acrylate (1 eq.) with γ-thiobutyrolactone (1 eq.) in the presence of 2 eq. of *n*-propylamine, at an acrylate concentration of 0.5 M in THF, at room temperature and under air atmosphere.

The spectral region from 1830 to 1490 cm^{-1} with high signal-to-noise ratio was selected for deconvolution, which has been performed separately for each reagent, the product and eventually reaction mixtures at different reaction times. Examples of the fit results are shown in Figure S 5, Figure S 6 and Table S 2.

Table S 2 - Band assignments and curve fit parameters of the FT-IR spectra in the spectral region of 1830-1490 cm^{-1} for the model reaction of *n*-butyl acrylate and γ-thiobutyrolactone with *n*-propylamine.

Vibration	Frequency (FWHH [b], Contour Shape) cm^{-1} (cm^{-1}, f_G)
νC=O (product)	1782 (11-14, 0.81)
νC=O (product)	1737 (18, 0.64)
νC=O (*n*-butyl acrylate)	1728 (16-18, 0.40)
νC=O (γ-thiobutyrolactone)	1714 (15, 0.54)
νC=O (H-bonded, γ-thiobutyrolactone)	1698 (22, 0.3)
Amide I (product)	1678 (17, 0.28)
Amide I (more strongly H-bonded, product)	1660 (19-24, 0.20)
νC=C (*n*-butyl acrylate)	1638 (11, 0.8)
νC=C (*n*-butyl acrylate)	1622 (14, 1)
δNH_2 (*n*-propylamine)	1614 (73, 1)
Amide II [a]	1540 (34-35, 0.81)

[a] The amide II vibration is constituted of different H-bonded vibrational sub-bands, but is deconvoluted for simplicity as one band.
[b] FWHH = Full Width at Half-Height

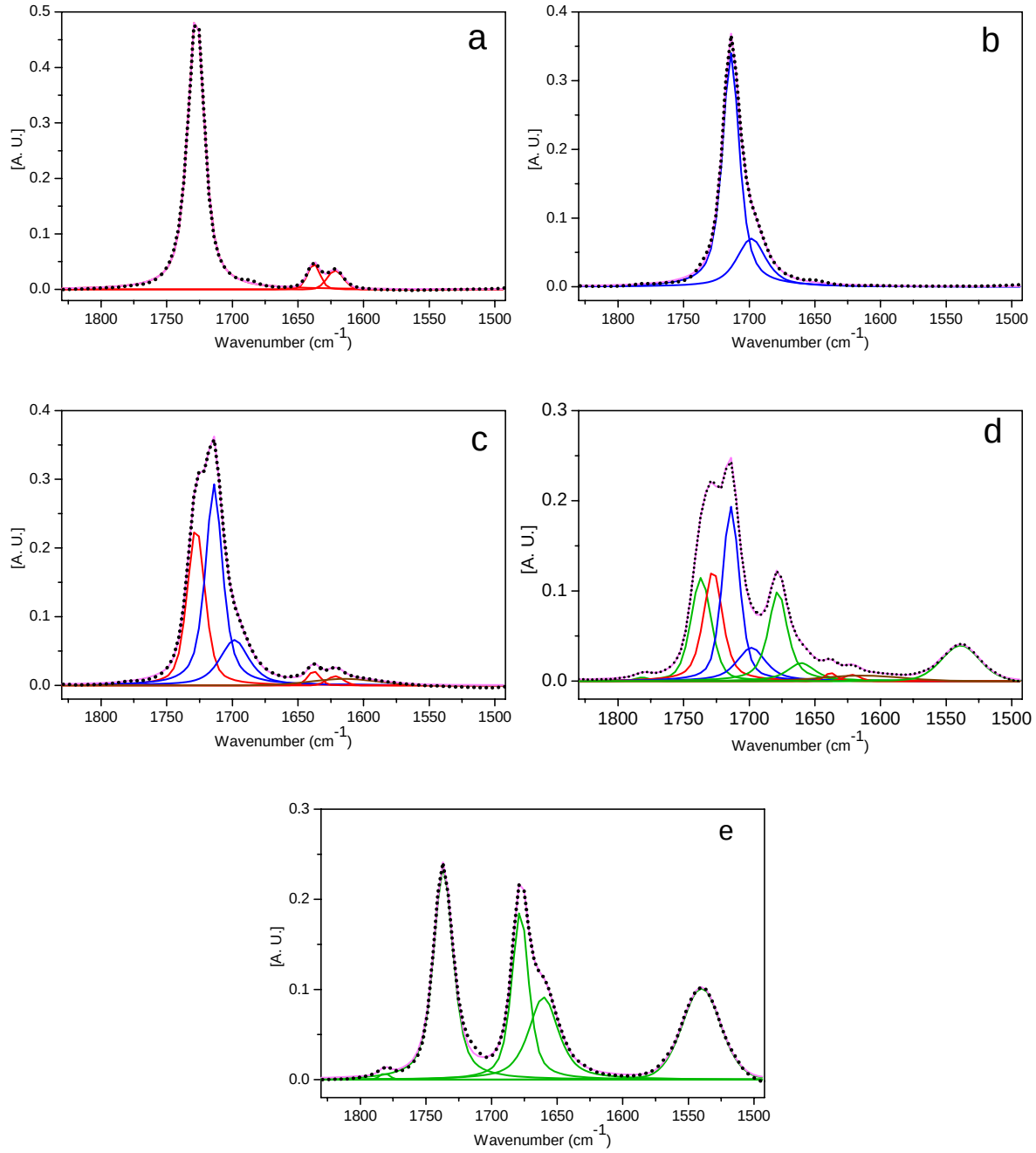


Figure S 5 - Curve fits of the FT-IR spectra measured in THF of (a) butyl acrylate, (b) γ-thiobutyrolactone, (c) the reaction mixture at t = 0, (d) the reaction mixture at t = 1 h, and (e) the formed product at t = 8 h. Reaction conditions: 1 eq. of butyl acrylate, 1 eq. of γ-thiobutyrolactone, 2 eq. of *n*-propylamine, acrylate concentration of 0.5 M in THF. The solid lines represent the fitted curves, while the dotted lines represent the measured spectra. In colors, red: butyl acrylate, blue: γ-thiobutyrolactone, brown: *n*-propylamine, green: product, pink: fitted sum spectra, and dotted black: measured spectra. See Table S 2 for the deconvoluted band positions, assignments and curve fit parameters.

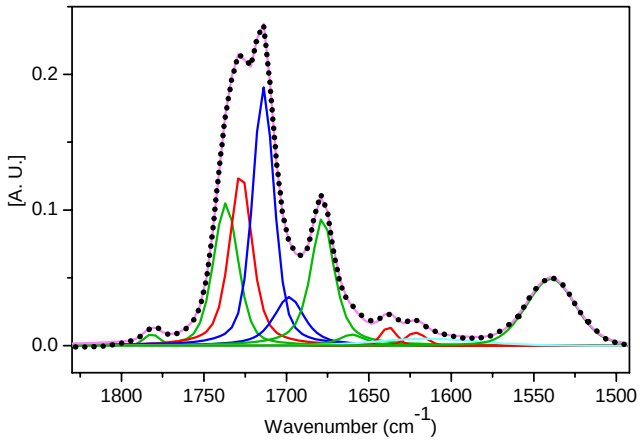


Figure S 6 - Curve fits of the FT-IR spectrum of the reaction mixture at t = 2 h for the reaction of *n*-butyl acrylate (1 eq.) with γ-thiobutyrolactone (1 eq.) in the presence of *n*-propylamine (1.1 eq.), at an acrylate concentration of 0.5 M in THF, at room temperature and under air condition. The solid lines represent the fitted curves, while the dotted lines represent the measured spectra. In colors, red: *n*-butyl acrylate, blue: γ-thiobutyrolactone, light blue: *n*-propylamine, green: product, pink: fitted sum spectra, and dotted black: measured spectra. See Table S 2 for the deconvoluted band positions and assignments and curve fit parameters. The deconvoluted data points at t = 2 h (Figure S 7) were extracted from Figure S 6.

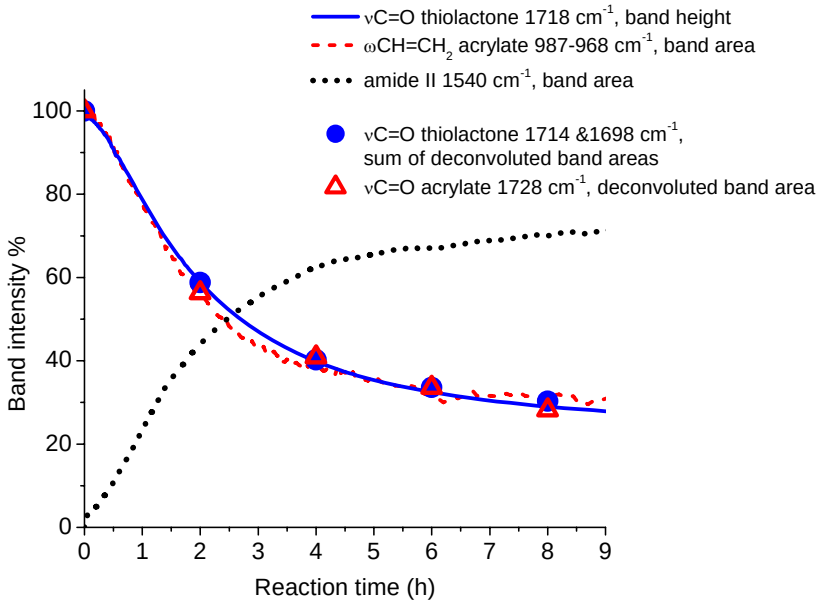


Figure S 7 - FT-IR band intensities as a function of reaction time for the model reaction of *n*-butyl acrylate (1 eq.) with γ-thiobutyrolactone (1 eq.) in the presence of 1.1 eq. of *n*-propylamine, at an acrylate concentration of 0.5 M in THF, at room temperature and under air condition. The relative amide II band area corresponding to 100 % conversion was determined from a similar experiment but with 2 eq. of *n*-propylamine where the thiolactone group was fully converted (*vide supra*).

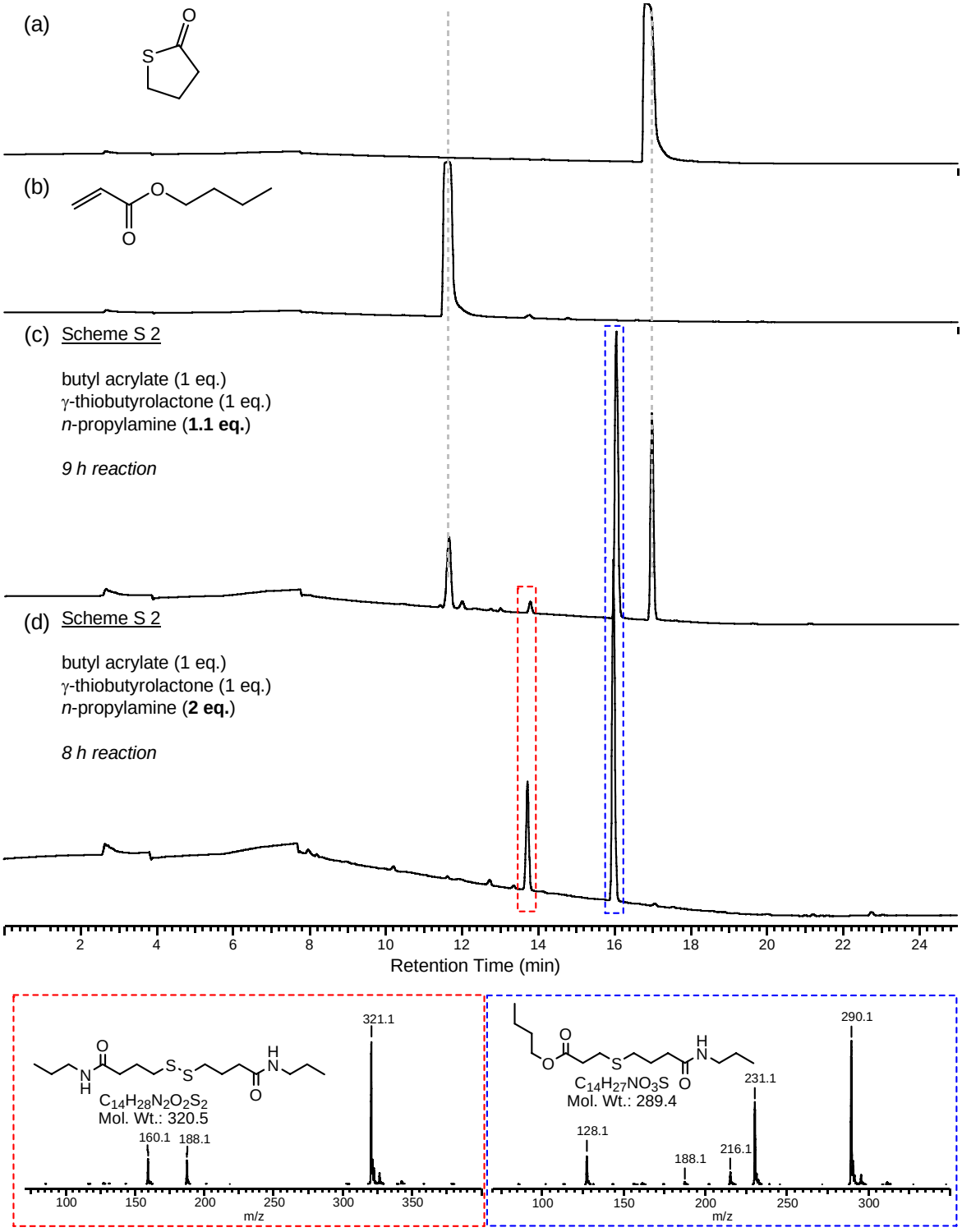


Figure S 8 - LC-MS analysis of the model reaction between butyl acrylate, γ-thiobutyrolactone and *n*-propylamine, at an acrylate concentration of 0.5 M in THF. Two different conditions were used; (c) 1.1 eq. of *n*-propylamine, 9 h reaction and (d) 2.0 eq. of *n*-propylamine, 8 h reaction. Inserts: ESI-MS spectra of relevant products of the model reaction.

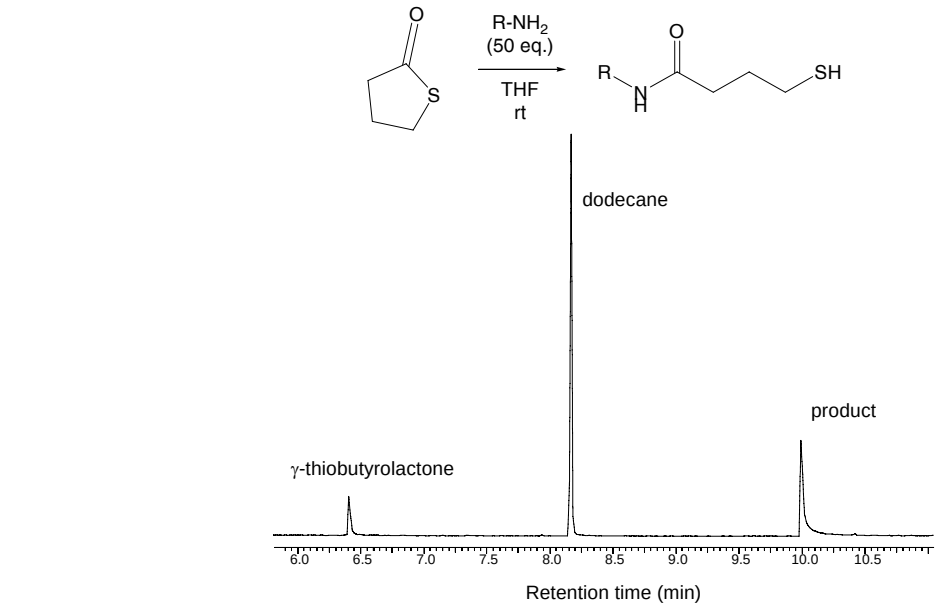


Figure S 9 - Kinetic screening of the aminolysis of γ-thiobutyrolactone under pseudo-first order kinetics. Conversion was monitored via *offline* GC analysis with dodecane as internal standard.

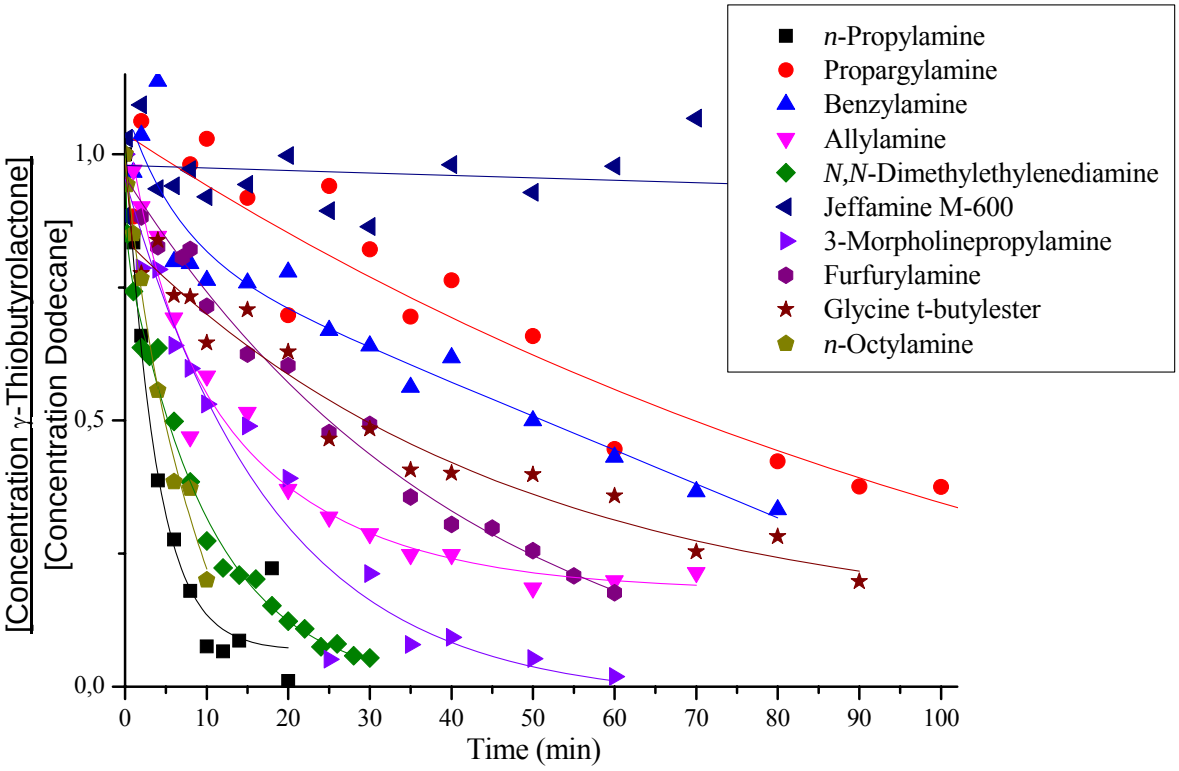
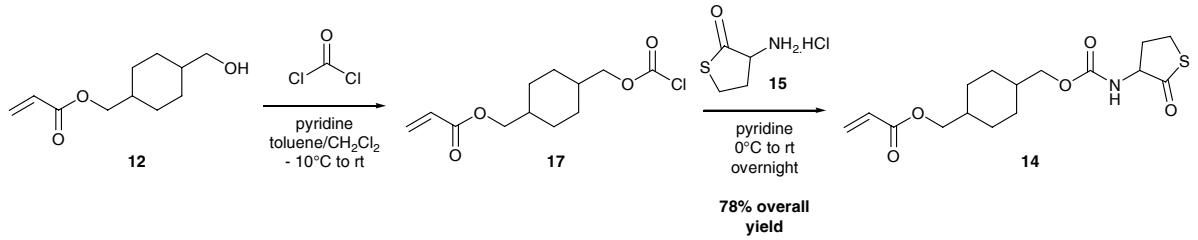


Figure S 10 - Normalized consumption of γ-thiobutyrolactone in the presence of different primary amines as a function of time.

Monomer synthesis



Scheme S 3 – One-pot two-step synthesis of the AB' monomer **14** from 1,4-cyclohexanedimethanol monoacrylate **12**.

1, 4 – Cyclohexanedimethanol monoacrylate **12** (mixture of *cis*/*trans* isomers, ratio 18/82, 33.368 g, 167.8 mmol) was dried by azeotropic distillation in the presence of toluene, subsequently dissolved in CH_2Cl_2 (100 mL) and pyridine (13.54 mL, 167.8 mmol). In a well-vented fume-hood, a solution of phosgene (~ 20 % in toluene, 100.0 mL, 193 mmol) was diluted with CH_2Cl_2 (100 mL) in a 3-neck 1-L flask and cooled to -10 °C. The solution of 1, 4 – cyclohexanedimethanol monoacrylate **12** was then added dropwise to the phosgene solution, while maintaining the reaction temperature below 0 °C. A white precipitate was formed during the addition and afterwards, the reaction was allowed to reach room temperature within the next 2 h. The excess of phosgene was removed by bubbling argon through the reaction mixture (the outlet was passed through a saturated solution of $NaHCO_3$ to quench the unreacted phosgene). The solution of the formed chloroformate **17** was cooled to 0 °C and treated with pyridine (27.08 mL, 335.6 mmol) and DL-homocysteinethiolactone hydrochloride **15** (25.780 g, 167.8 mmol). The reaction mixture was allowed to reach room temperature overnight. The brown mixture was evaporated in the presence of 200 mL silicagel to dryness and directly purified by column chromatography (gradient elution: 100 % CH_2Cl_2 → CH_2Cl_2 / acetone: 95 / 5). The slightly coloured fractions were concentrated, redissolved in a minimal amount of CH_2Cl_2 and precipitated in iso-octane, yielding the AB'-monomer **14** as a white solid with an overall yield of 78 % (45.10 g).

$C_{16}H_{23}NO_5S$ (341.4); m/z (ESI-MS) 342.1 $[M+H]^+$.
HRMS: $[M+H]^+$ Expected 342.1370, Found 342.1371; $[M+NH_4]^+$ Expected 359.1635, Found 359.1636.

^{1}H-NMR (500 MHz, $CDCl_3$, ppm) δ 6.38 (*dd*, 1H, 17.4, 1.5 Hz), 6.11(*dd*, 1H, 17.4, 10.5 Hz), 5.81 (*dd*, 1H, 10.4, 1.5 Hz), 5.14 (*br s*, 1H), 4.31 (*m*, 1H), 4.06_{cis}/3.97_{trans} (*d*, 2H, 7.2_{cis} / 6.5_{trans} Hz), 4.01_{cis}/3.91_{trans} (*m*, 2H), 3.33 (*ddd*, 1H, 12.1, 11.5, 5.1 Hz), 3.23 (*ddd*, 1H, 11.4, 7.0, 1.1 Hz), 2.87 (*m*, 1H), 2.00 (*m*, 1H), 1.83_{cis}/1.61_{trans} (*m*, 2H), 1.81_{trans}/1.52_{cis} (*m*, 4H), 1.42_{cis}/1.00_{trans} (*m*, 4H).

^{13}C-NMR (125 MHz, DMSO-d_6, ppm) δ 205.6 (C), 165.5 (C), 156.2 (C), 131.4 (CH_2), 128.5_{trans} / 128.4_{cis} (CH), 68.9 (CH_2), 68.7_{trans}/66.7_{cis} (CH_2), 59.8 (CH), 37.0_{trans}/34.3_{cis} (CH), 36.6_{trans}/34.1_{cis} (CH), 29.79 (CH_2), 28.2_{trans}/24.7_{cis} (4 x CH_2), 26.32 (CH_2).

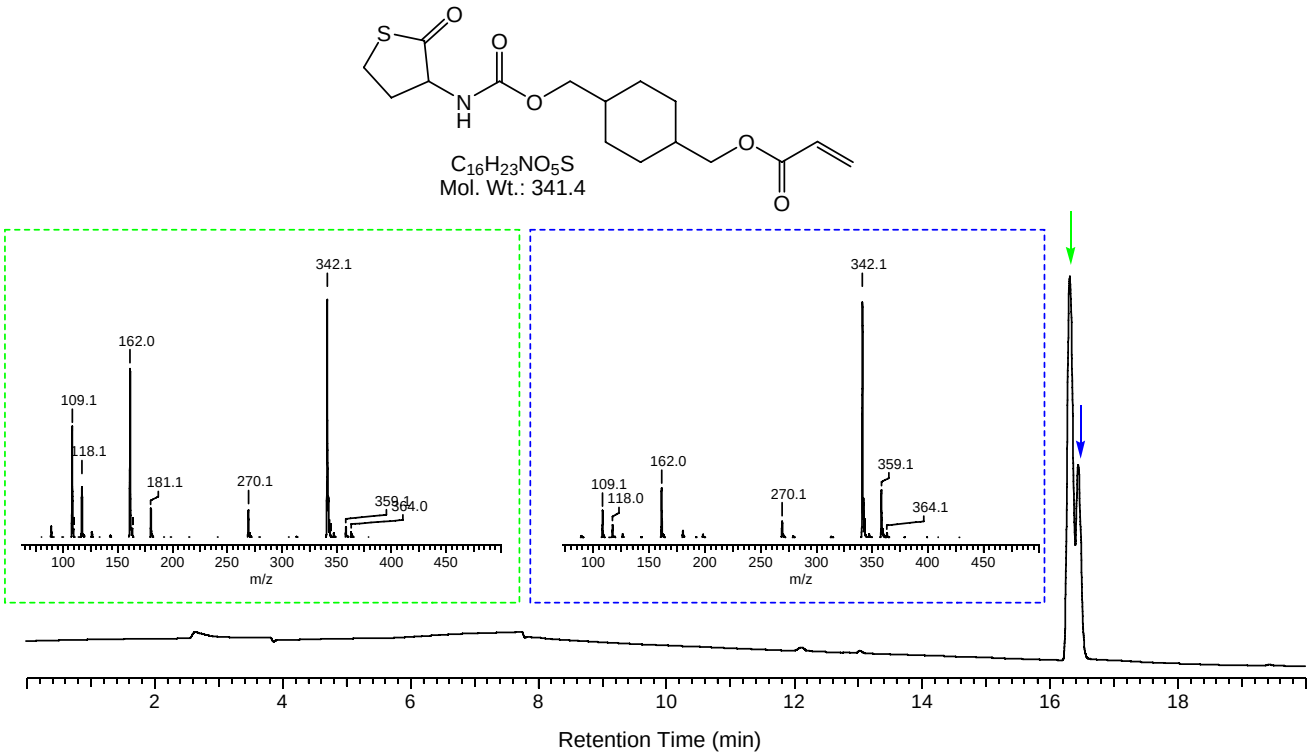


Figure S 11 - LC-MS analysis of the purified AB'-monomer **14**. The two peaks represent the *cis*- and *trans*-isomer, having the same ESI-MS-trace (inserts).

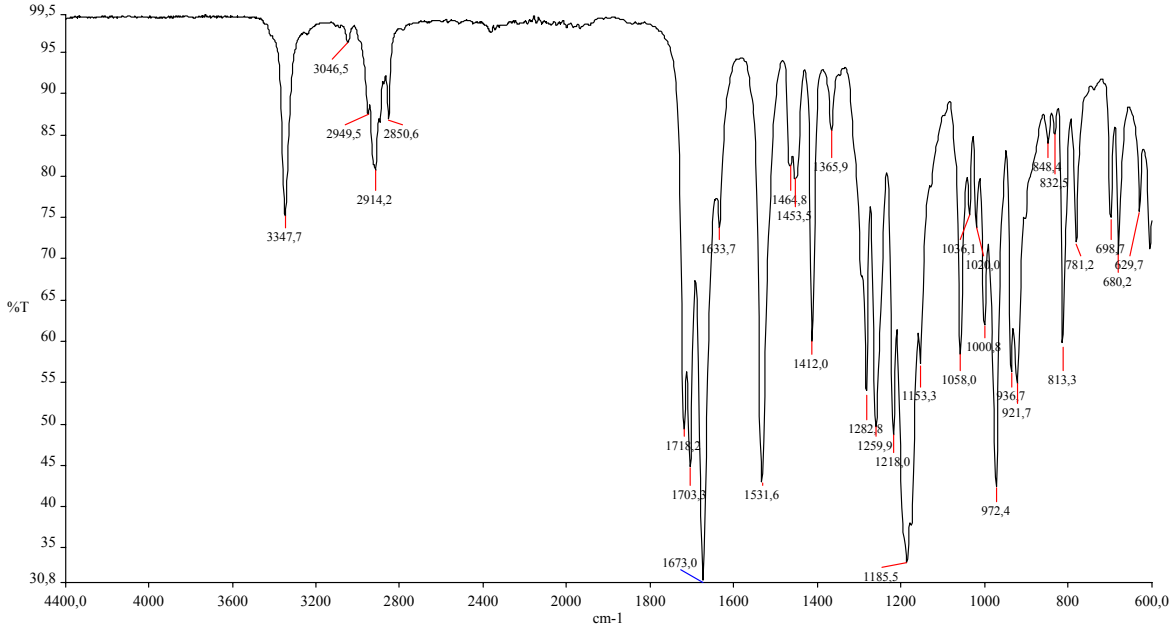


Figure S 12 - IR (ATR) analysis of the purified AB'-monomer **14**. The peak assignment is summarized in Table S 3.

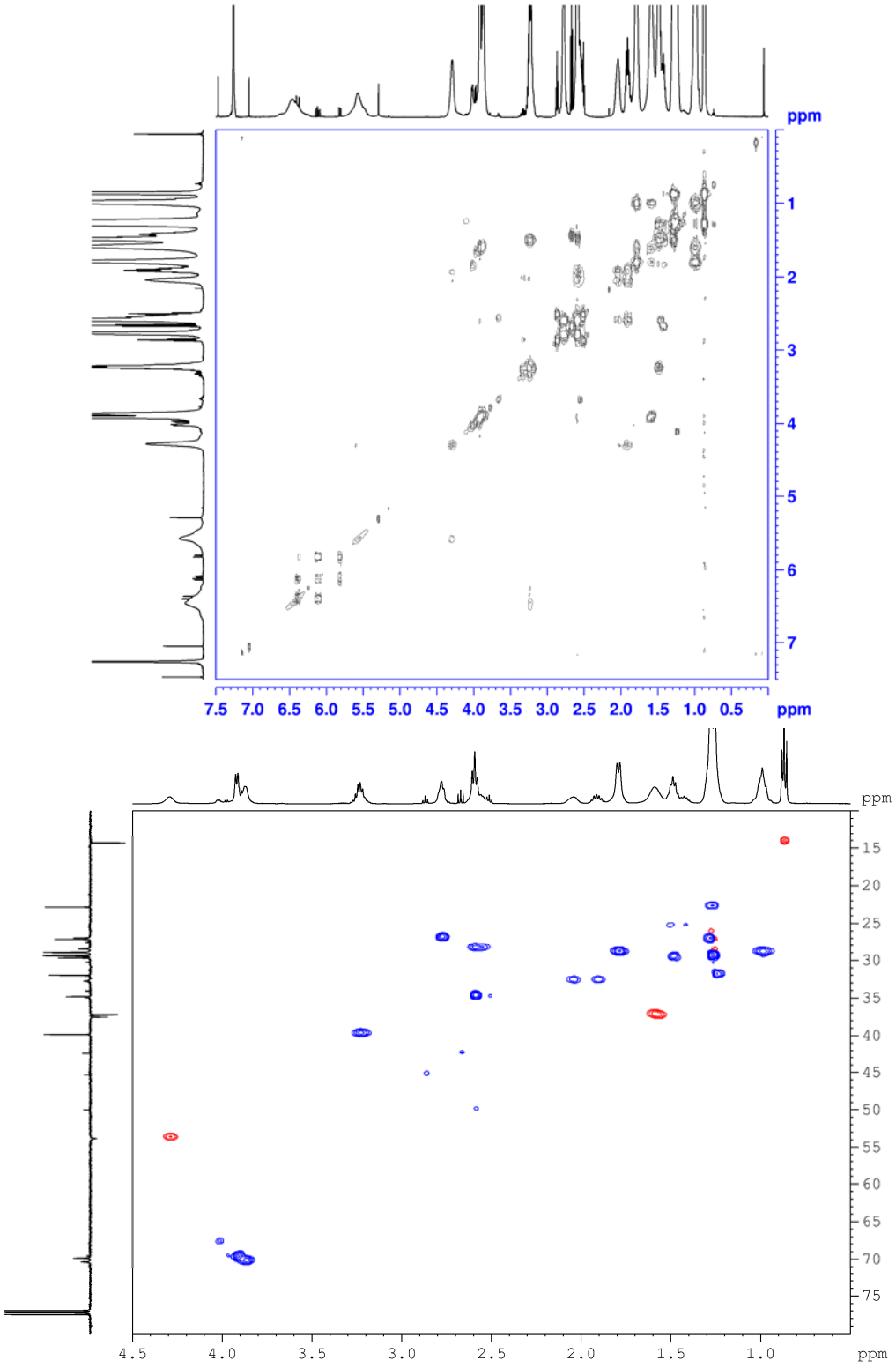


Figure S 13 – 2D-NMR analysis ($CDCl_3$, 500 MHz) of polymer **18**: COSY (*top*) and HSQC (*bottom*) facilitates the assignment of the peaks in the 1D-^{1}H-NMR spectrum (Scheme 5).

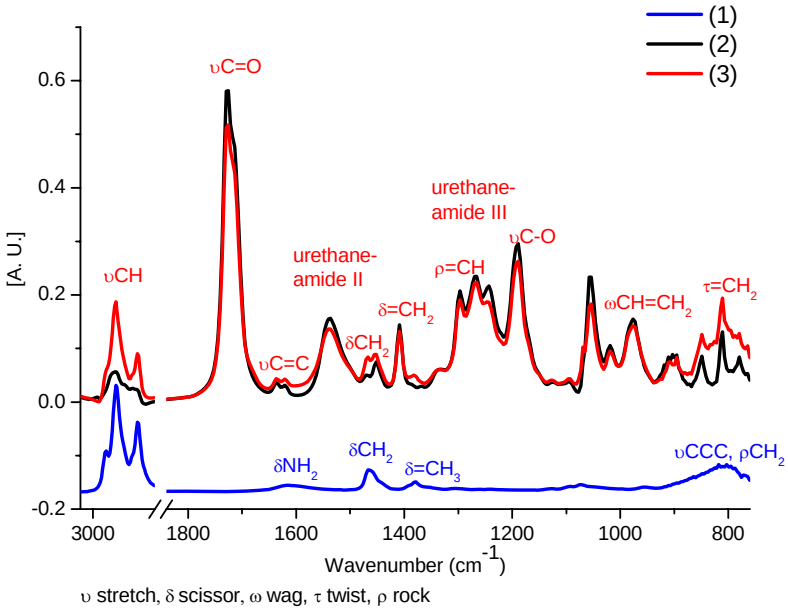


Figure S 14 - FT-IR spectra recorded for (1) neat *n*-octylamine and the reaction of 1 eq. of monomer **14** with 1.1 eq. of *n*-octylamine at a monomer concentration of 0.5 M in THF, at room temperature and under air condition: (2) prior and (3) right after addition of *n*-octylamine.

Table S 3 - Observed vibrational frequencies (cm^{-1}) and spectral assignments for the reaction of 1 eq. of monomer **14** with 1.1 eq. of *n*-octylamine in THF.

Monomer **14**		*n*-octylamine	
Wavenumber (cm^{-1})	Assignment[a]	Wavenumber (cm^{-1})	Assignment[a]
1727-1713	ν(C=O) urethane, acrylate and thiolactone	1600	NH_2 symmetric deformation
1636, 1620	ν(C=C)	1465	CH_2 deformation
1537	urethane-amide II	1377	CH_3 deformation
1468, 1452	δ(CH_2)	910-700	CCC stretch, CH_2 rock, NH_2 wag
1409	δ(=CH_2)		
1380	δ(CH_3)		
1296, 1267	ρ(=CH)		
1244	urethane-amide III		
1187	ν(C-O)		
975	ω(CH=CH_2)		
810	τ(=CH_2)		

formed polymer	
Wavenumber (cm^{-1})	Assignment[a]
1731	ν(C=O) (urethane & ester)
1680	amide I (νC=O, νC-N) of the amide bond formed
1537	amide II (δN-H, νC-N) of urethane and the amide formed
1240	amide III of urethane and the amide formed

ν stretch, δ scissor, ω wag, τ twist, ρ rock

[a] Assignments from reported vibrational studies[2-7] were compared to assign the bands observed in the experimental spectra.

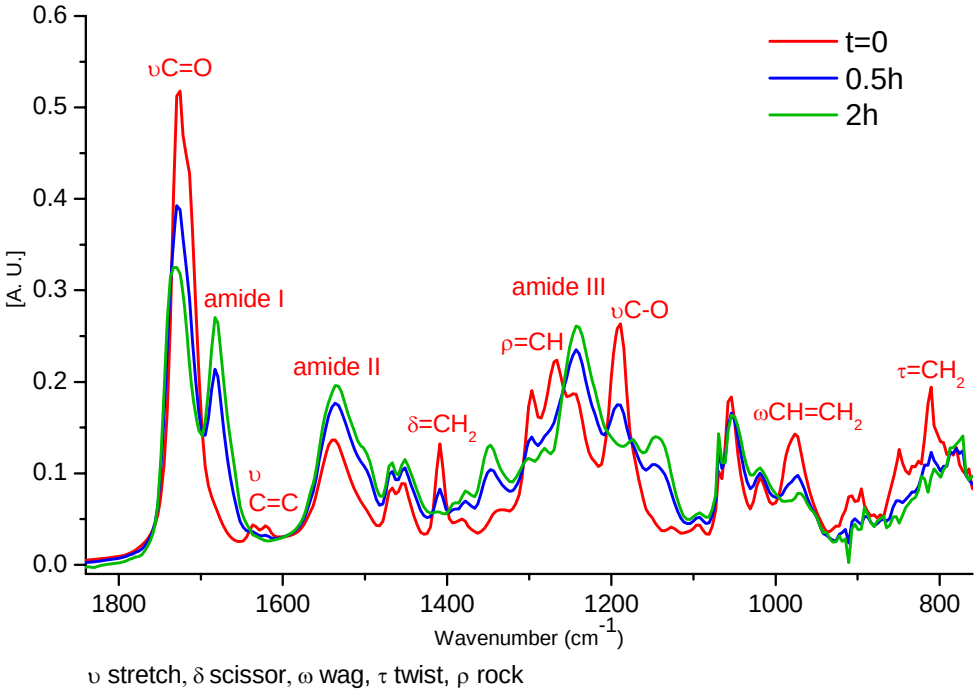


Figure S 15 - FT-IR spectra as a function of reaction time recorded for the reaction of 1 eq. of monomer **14** with 1.1 eq. of *n*-octylamine at a monomer concentration of 0.5M in THF, at room temperature and under air condition.

Due to the overlapping of the urethane, acrylate and thiolactone C=O vibrations, the thiolactone ring-opening accompanied by amide bond formation was followed by the intensity of the amide I vibrational band at 1680 cm^{-1}; whereas the conversion of the acrylate double bond was monitored by the scissoring acrylate vibration at 1409 cm^{-1}. Deconvolution and curve fitting of the spectra in the region of 1800-1380 cm^{-1} were performed in a similar manner to that for the model reactions (i.e. the reaction of *n*-butyl acrylate and γ-thiobutyrolactone and *n*-propylamine), in which curve fits were performed separately for each reagent and the final product and eventually for the reaction mixture at a certain reaction time. The fit parameters (frequency, FWHH and contour shape) of the vibrations corresponding to the thiolactone and acrylate moieties of the monomer **14** were fitted based on the fit values of the *n*-butyl acrylate and γ-thiobutyrolactone model compounds. The fit parameters obtained from the fitting of the starting monomer and final polymer product were fixed during the fitting procedure. Table S 4 shows the assignments and curve fit parameters of the deconvoluted bands. Examples of the fit results are shown in Figure S 10. The areas of the deconvoluted amide I bands at 1682 and 1636 cm^{-1} and the scissoring acrylate vibration at 1409 cm^{-1} were chosen for estimation of the reaction conversions because these bands are well separated from the others giving the most reliable fit values. However, it should be noted that there could be a certain error, although expected to be not significant, for the use of the area sum of the two fitted amide I bands as a measure for the amide group formation, due to possible different absorption coefficients of these bands as well as possible change in their content ratio during the reaction.

Table S 4 - Band assignments and curve fit parameters of the FT-IR spectra in the spectral region of 1800-1380 cm^{-1} for the reaction of 1 eq. of the monomer **14** with 1.1 eq. of *n*-octylamine in THF.

Vibration	Frequency (FWHH[b], Contour Shape) cm^{-1} (cm^{-1}, f_G)
νC=O (ester of product)	1740 (17, 0.60)
νC=O (urethane)	1729 (19, 0.43)
νC=O (acrylate)	1728 (16, 0.40)
νC=O (ester of product)	1718 (15, 1)
νC=O (thiolactone)	1714 (16, 0.44)
νC=O (more strongly H-bonded, urethane and thiolactone)	1705-1704 (19-21, 0.7)
Amide I (product)	1682 (20, 1)
Amide I (more strongly H-bonded, product)	1666 (25, 0.61)
νC=C (acrylate)	1635 (10, 1)
νC=C (acrylate)	1621 (11, 1)
δNH_2 (*n*-octylamine)	1600 (66, 1)
Amide II[a] (urethane and amide bond formed in the product)	1537 (42, 1)
Amide II[a] (more strongly H-bonded)	1500 (30, 1)
$\delta(CH_2)$	1469 (10-11, 1)
$\delta(CH_2)$	1453 (22-27, 0.75)
$\delta(=CH_2)$	1409 (11, 0.15)
$\delta(CH_3)$	1380-1382 (18-22, 1)

[a] The amide II vibration is contributed by both the urethane vibration and the amide bond formed as a result of the thiolactone ring-opening, but for simplicity is deconvoluted as one sum-band.
[b] FWHH = Full Width at Half-Height

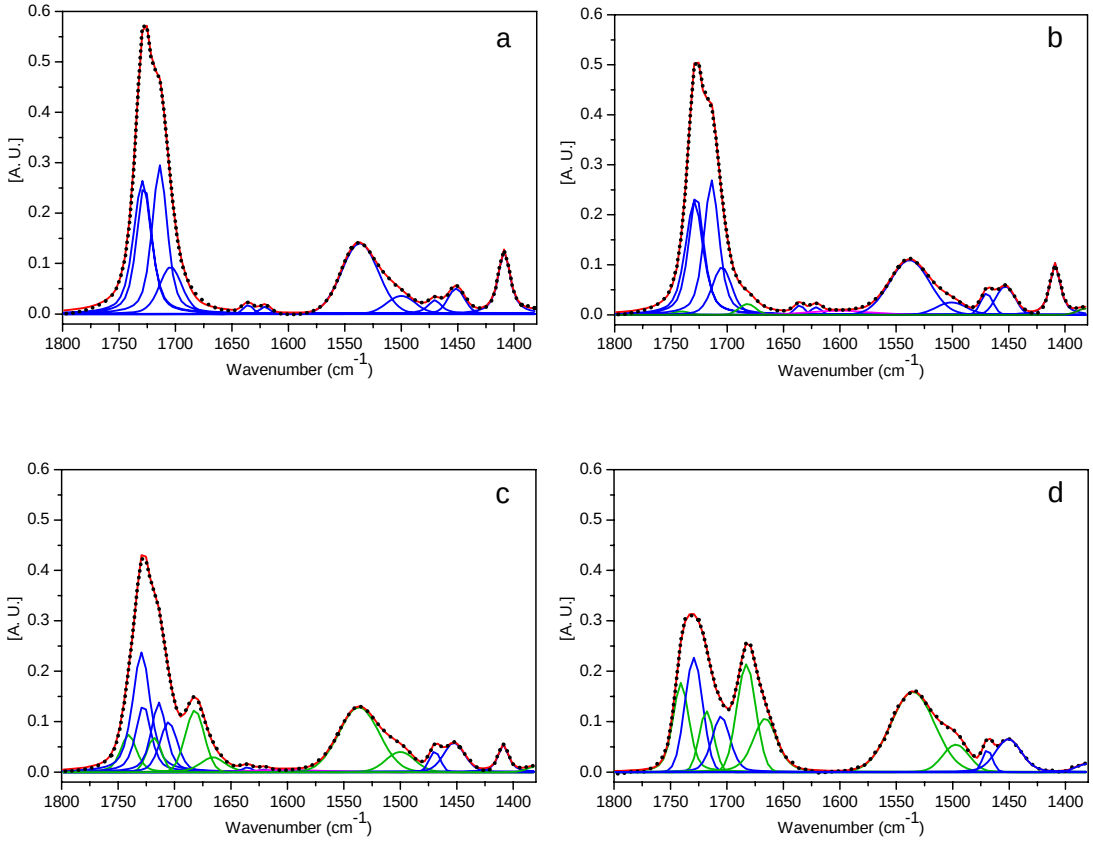


Figure S 16 - Curve fits of the FT-IR spectra measured in THF of (a) monomer **14**, and of [monomer **14** + *n*-octylamine] reaction mixture at (b) t = 0, (c) t = 15 min, and (d) the polymer product at t = 3 h. Reaction conditions: 1 eq. of monomer **14**, 1.1 eq. of *n*-octylamine, monomer concentration of 0.5 M, room temperature. The solid lines represent the fitted curves, while the dotted lines represent the measured spectra. In colors, blue: monomer **14**, pink: *n*-octylamine, green: product, red: fitted sum spectra, and dotted black: measured spectra. See Table S 4 for deconvoluted band positions and assignments and curve fit parameters.

Polymerization by amine-thiol-ene conjugation: general protocol

The monomer **14** (341 mg, 1.0 mmol) was dissolved in THF (2.0 mL). The primary amine (1.1 mmol) was added at room temperature and the clear reaction mixture was stirred for 24 h at ambient conditions. The polymer was collected by precipitation in cold diethyl ether, washed with cold diethyl ether and cold methanol and dried prior to analysis.

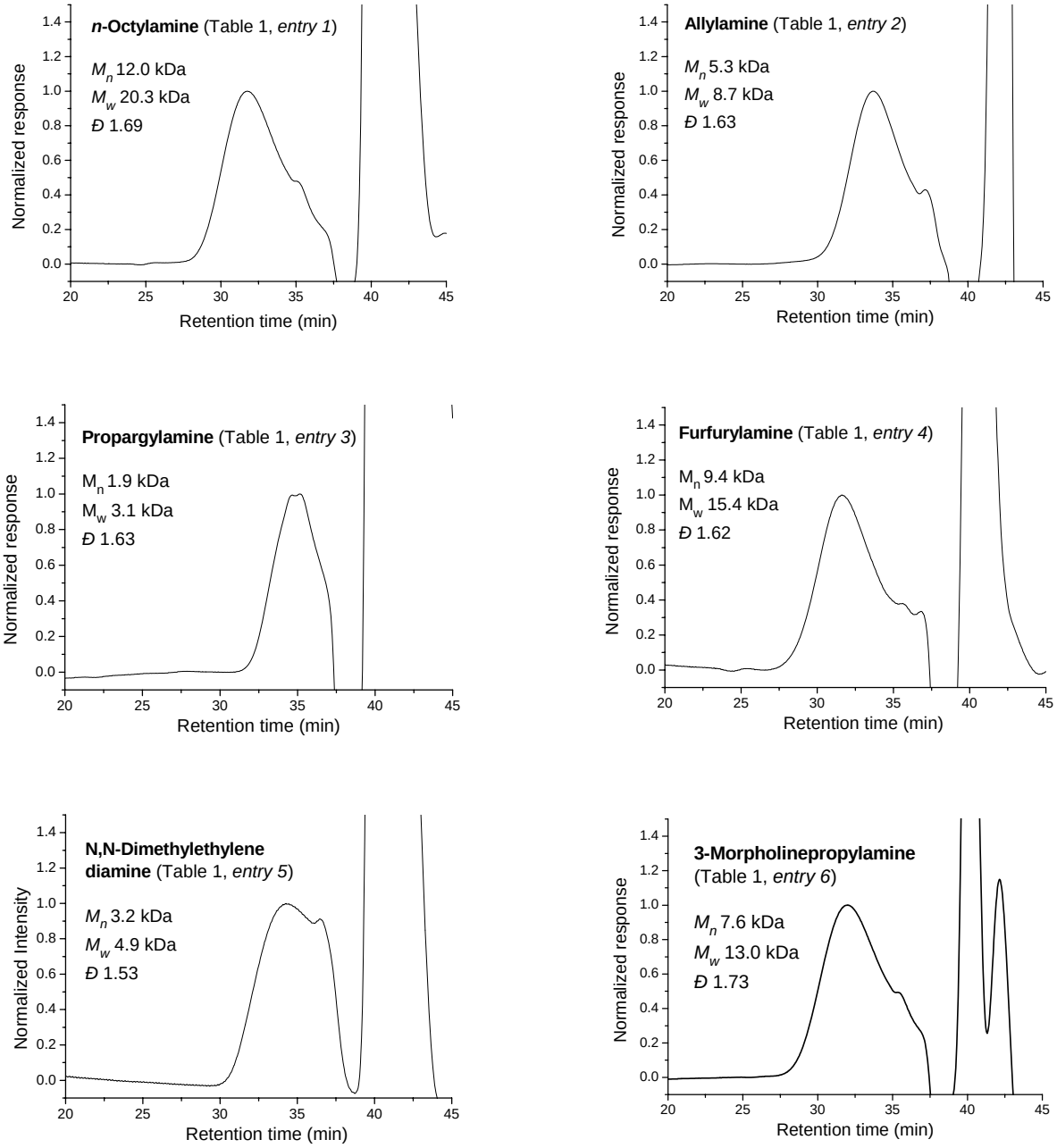


Figure S 17 - SEC traces and distribution analysis of the obtained polymers via treatment of monomer **14** with six primary amines (Table 1, *entries 1→ 6*).

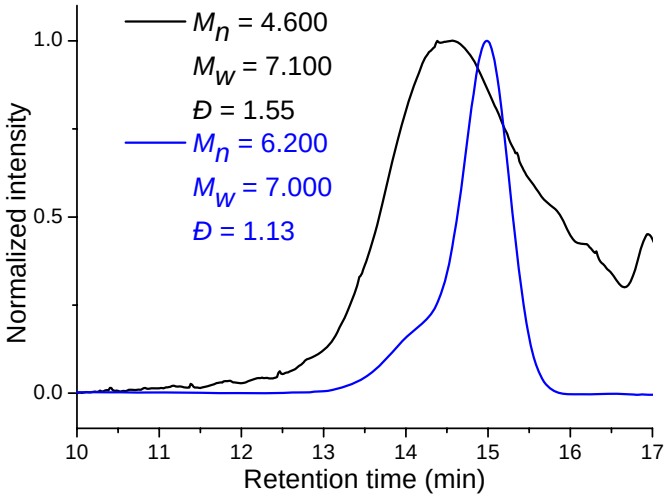


Figure S 18 - SEC traces (THF as eluent) of allyl-containing PU (Table 1, *entry 2*) ***before*** and ***after*** preparative SEC. The narrow-disperse fraction was subsequently analyzed by MALDI-TOF (Figure 3).

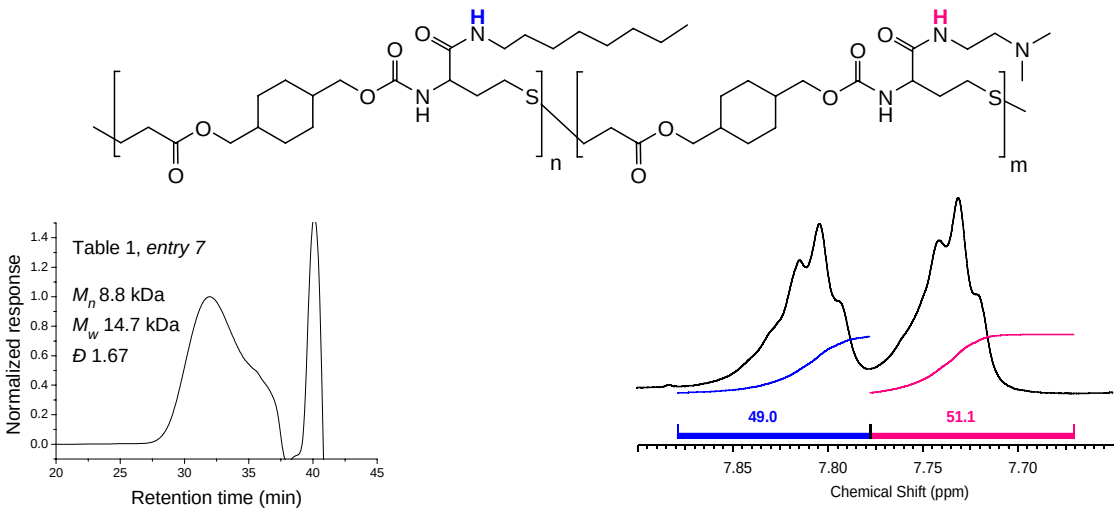


Figure S 19 - Synthesis of PUs having multiple functionalities along the backbone by treatment of monomer **14** with a combination of *n*-octylamine and *N*,*N*-dimethylethylene diamine (Table 1, *entry 7*). SEC trace (*bottom left*) and ^{1}H-NMR detail ($CDCl_3$, 500 MHz) including the integration of relevant signals determining the ratio of the incorporated amines (*bottom right*).

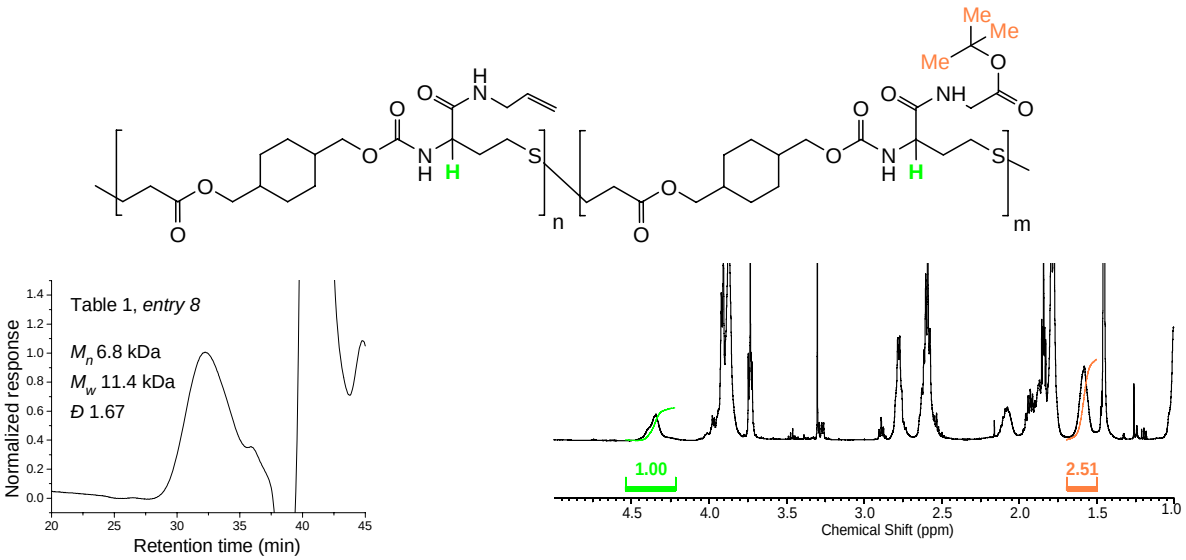


Figure S 20 - Synthesis of PUs having multiple functionalities along the backbone by treatment of monomer **14** with a combination of allylamine and glycine t-butylester (Table 1, *entry 8*). SEC trace (*bottom left*) and ^{1}H-NMR detail ($CDCl_3$, 500 MHz) including the integration of relevant signals determining the ratio of the incorporated amines (*bottom right*).

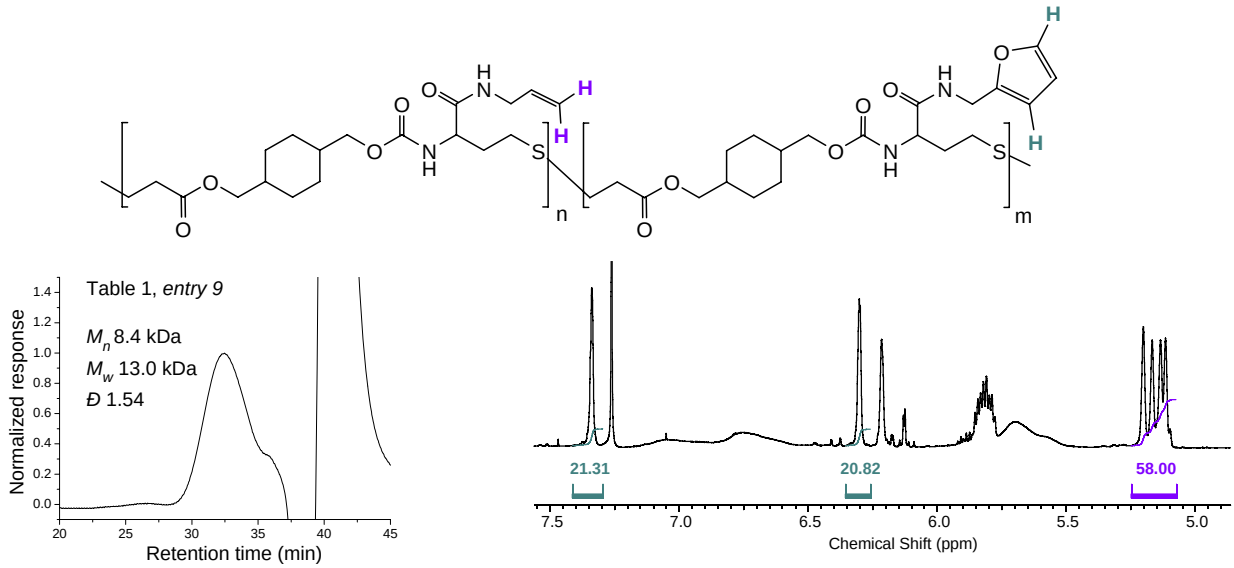


Figure S 21 - Synthesis of PUs having multiple functionalities along the backbone by treatment of monomer **14** with a combination of allylamine and furfurylamine (Table 1, *entry 9*). SEC trace (*bottom left*) and ^{1}H-NMR detail ($CDCl_3$, 500 MHz) including the integration of relevant signals determining the ratio of the incorporated amines (*bottom right*).

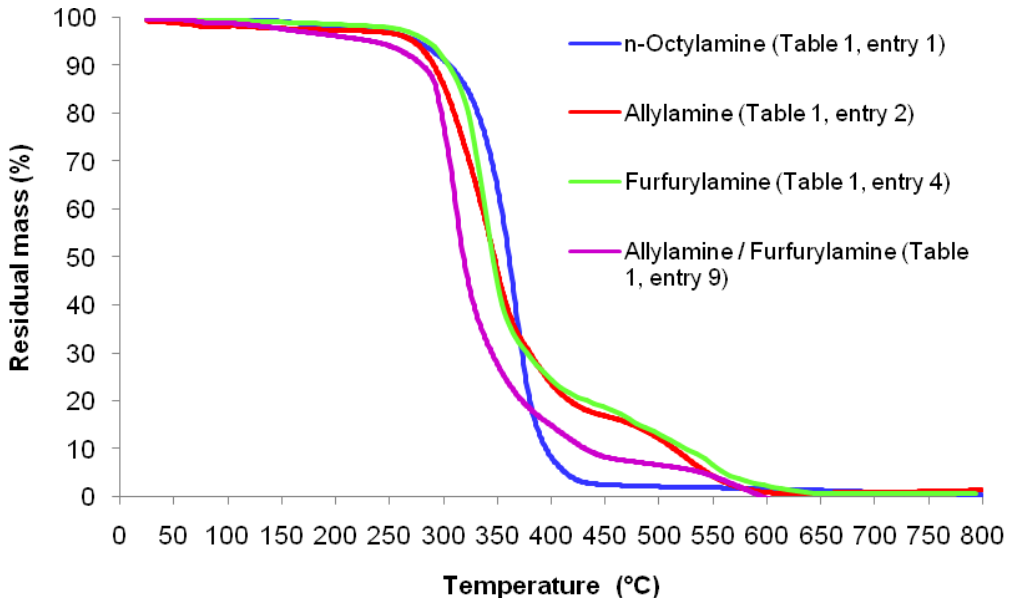


Figure S 22 - TGA-analysis of the polymers made via amine-thiol-ene conjugation.

Post-polymerization modification

Thiol-ene modification of allyl-containing PU (Figure 4)

Monomer **14** (0.5 mmol; 170.7 mg) was dissolved in THF (1.0 mL). Allylamine (0.55 mmol; 0.038 mL) was added and the reaction mixture was stirred at room temperature for 24 h. A sample was taken from the clear reaction mixture for SEC- and ^{1}H-NMR-analysis. Consequently, thiol-ene modification was performed in the same pot by adding 1-octanethiol (1.0 mmol, 0.180 mL) and DMPA (0.04 mmol, 10.0 mg) as photo-initiator and irradiating UV-light (365 nm) for 5 h. Again, a sample was taken from the clear reaction mixture for SEC- and ^{1}H-NMR-analysis.

Furan-maleimide modification of furan-containing PU (Figure S 23)

Monomer **14** (1.0 mmol; 341.42 mg) was dissolved in THF (2.0 mL). Furfurylamine (1.0 mmol; 0.088 mL) and allylamine (1.0 mmol; 0.075 mL) were added and the reaction mixture was stirred at room temperature for 24 h. 500 µL was taken out of the reaction mixture and precipitated in 5 mL cold Et_2O. The precipitate was then washed with cold MeOH (3 x 10 mL) and dried under vacuum. The purified sample was analyzed by SEC- and ^{1}H-NMR.

To the remaining 1.5 mL, *N*-methylmaleimide (1.5 mmol; 166.7 mg) was added. The reaction mixture was stirred at 50 °C for 5 h. 500 µL was again taken out of the reaction mixture and was precipitated in 5 mL cold Et_2O. The yellow precipitate was washed with cold MeOH (3 x 5 mL) and then dried under vacuum. The purified sample was analyzed by SEC- and ^{1}H-NMR

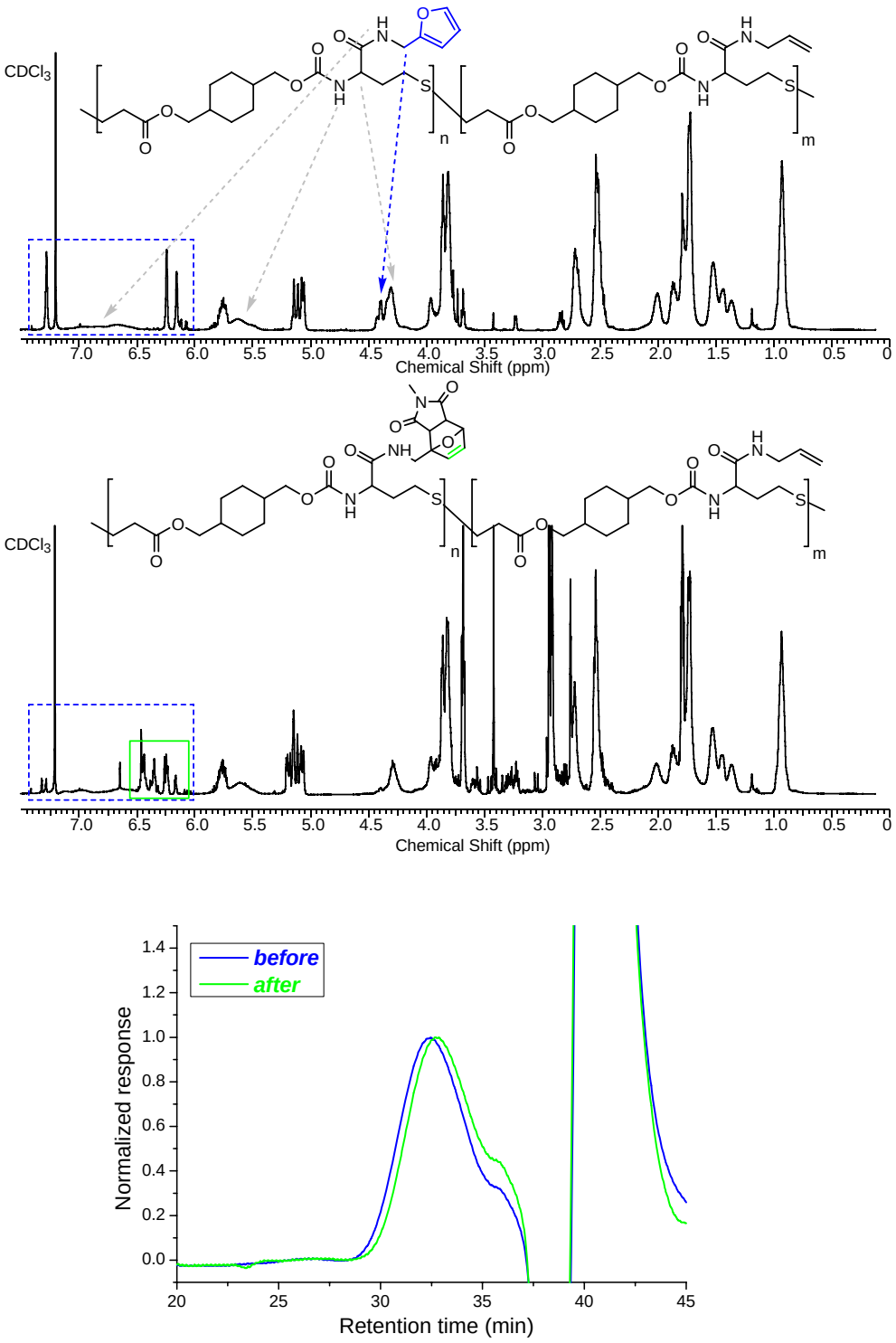


Figure S 23 - Post-polymerization modification in the same medium of the furfuryl-containing PUs by Diels-Alder reaction with *N*-methylmaleimide. (Top) Details of ^{1}H-NMR spectra ($CDCl_3$, 500 MHz) after poly-addition and after subsequent Diels-Alder modification. (Bottom) Corresponding SEC traces of reaction samples before and after modification.

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