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Polymer Up-Cycling by Mangana-Electrocatalytic C(sp3)–H Azidation without Directing Groups

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1. Materials and Methods

Mangana-electrocatalyzed C–H azidation were performed under an atmosphere of nitrogen, in undivided electrochemical cells (10 mL) using pre-dried Schlenk tubes. Acetonitrile (MeCN) was stored over activated 3 Å molecular sieve. 1,2-Dichlorbenzene (1,2-DCB), MeCN and glacial acetic acid (AcOH) were degassed by freeze-pump-thaw. Metallosalen complexes were synthetized according to previously described methods.[1, 2] Polystyrene with a M_n of 32 kDa and narrow disperse polystyrene with a M_n of 16 kDa were prepared according to literature procedures.[3, 4] *N*, *N*, *N'*, *N''*, *N''*-Pentamethyldiethylentriamin (PMDTA) and other chemicals were obtained from commercial sources and were used without further purification. Platinum electrodes (10 mm x 15 mm x 0.125 mm, 99.95%; obtained from ESG-Edelmetall-Handel GmbH & Co. KG) and graphite felt electrodes (10 mm x 15 mm x 6 mm, for 6 mL reaction volume or 10 mm x 15 mm x 3 mm, for 3.5 mL reaction volume, SIGRACELL GFA 6 EA, obtained from SGL Carbon, Wiesbaden, Germany) were connected using stainless steel adapters. Electrocatalysis was conducted using an Metrohm Autolab potentiostat in constant current mode. Narrow standard polystyrene (PS) was purchased from PSS waters and used as received. NMR: ^{1}H-, ^{13}C-, HSQC- and HMBC-spectra were recorded on Varian 500 MHz, Bruker 400 MHz and Bruker 600 MHz spectrometers in CD_2Cl_2 (^{1}H NMR: 5.32 ppm; ^{13}C NMR: 53.84 ppm), $CDCl_3$ (^{1}H NMR: 7.26 ppm; ^{13}C NMR: 77.16 ppm) or THF-d_8 (^{1}H NMR: 3.58, 1.73 ppm; ^{13}C NMR: 67.57, 25.37 ppm), chemical shifts (δ) are given in ppm. High temperature NMR were recorded on a Varian 500 MHz spectrometer at 75 °C in deuterated tetrachloroethane $C_2D_2Cl_4$ (^{1}H NMR: 6.00 ppm; ^{13}C NMR: 74.20 ppm). ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, m = multiplet, br = broad signal), coupling constant (Hz), and assignment. GPC: Gel permeation chromatography (GPC) was performed at 30 °C in THF 1.0 mL/min fitted with two SDV analytical columns (10^3 Å, 10^4 Å; Polymer Standard Service) and a JASCO-4030 refractive index detector. The sample was dissolved in tetrahydrofuran (THF) (ca. 1.5 mg/mL) at room temperature and the resulting solution was injected for GPC analysis. The mass average molar mass (M_w) and polydispersity index ($Đ$) are reported against narrow-disperse polystyrene standards (PSS, ReadyCal-kit Poly(styrene), M_p 370 – 2520000 Da, Lot No.: pskitr1-10, Part No.: PSS-pskitr1). IR: All spectra were recorded on a Bruker FT-IR Alpha device as a solid or a thin film obtained after solvent evaporation from a dichloromethane (DCM) or THF polymer solution and were averaged over 32 scans, smoothed and baseline corrected. DSC: Differential scanning calorimetry (DSC) was used to determine the glass transition temperature of the polymers using a Netzsch DSC Instrument. For polymer samples, DSC measurements were performed on 10 mg sample in Tzero pans. The samples underwent a heat, cool, heat cycle with a temperature ramp rate of 10 C/min. Data were reported from the second heating cycle. TGA: Thermogravimetric analysis (TGA) was performed on a Netzsch TG 209 F1 Instrument at a heating rate of 20 C/min. Elemental analysis was performed on a Elementar 4.1 vario EL 3. For elemental analysis the sample was dissolved in DCM or tetrachloroethane and reprecipitated from MeOH. The collected solids were dried *in vacuo* for 12 h. The trace metal analysis was performed on a Thermo Scientific™ iCAP™ RQ ICP-MS. Trace metal grade HNO_3 was obtained from Thermo Scientific. LC-MS grade water was used for sample dilution.

Caution: Experimentation with Organic Azides.

Although the authors did not observe safety concerning incidents during experimentation, we would like to highlight the special safety consideration for any experimentation with organic or inorganic azide compounds as they can be considered as often toxic and potentially explosive chemicals that can decompose under external impact such as heat, pressure, shock. For safety, thus all reactions and processing steps involving sodium azide should be carried out behind a blast shield.

The mol per euro in Figure 1 were calculated using following data:

Table S1: Mol per euro.

Oxidant	Formula	Supplier (grade, size)	M/ g mol^{-1}	Price per gram/ € g^{-1}	Price per Mol/ € mol^{-1}
PIDA	(M*(price per gram))	Chem-Impex International Inc. (99%, 5 kg)	322.10	0.305	98.24
$Cu(OAc)_2$* H_2O	(M*(price per gram))	Chem-Impex International Inc. (99%, 100 kg)	181.63	0.039	7.07
H_2O_2	(M*(price per gram))	Chem-Impex International Inc. (Food grade, 35%, 1 Gal)	34.02	0.15	5.20
O_2	(price per L, bar/*n*)	AIR Liquide (2.5, 50 L; 300 bar)	605.43 mol [a]	-	0.23[b]
Electricity[c]	(Price per kWh/Mol per kWh)	Average price in Germany (since 07.2022) [d]	2.89 kWh mol^{-1}	0.327 € kWh^{-1}	0.11

[a] O_2 is approximated as an ideal gas; the mole *n* of the cylinder were calculated using $n = pV/(RT)$, with $p = 3*10^7$ Pa, $V = 5*10^{-2}$ m^3, R = 8.314 (Pa*m^3)/(K*mol) and $T = 298$ K. [b] The price for a 2.5, 50 L, 300 bar cylinder from AIR Liquide is 138.50 € (https://www.linde-gas.de/shop/de/de-ig/sauerstoff-25-sauerstoff-25, accessed on 08.09.2022). [c] The price of electricity depends on the reaction conditions as current, and potential varies under constant current conditions. Thus, the maximum observed potential U_{max} of 3.0 V under the optimized conditions was used for calculation of mol per Wh using $I = 4.0*10^{-3}$ A, $t = 2.5$ h electrolysis time, using following formular $E/n = U_{max}*I*t*F$. [d] The average price for electricity is 32.7 ct/kWh in Germany (https://strom-report.de/strompreise/, accessed on 23.08.2022).

2. IR-Analysis and Calculation of the Level of Functionalization

To obtain data for comparing the azide incorporation by relative IR intensity following approximations were applied. First the absorption of a given functional group was approximated by the Lambert-Beer-Law (Eq.1):

$$A = \varepsilon d c \ (\text{Eq.1})$$

To avoid deviation in thickness *d* of the sample, the ratio of the absorption azide band (2106 cm^{-1}) and the benzylic C–H band (3026 cm^{-1}) was formed (Eq.2):

$$\frac{A_{N_3}}{A_{CH}} = \frac{\varepsilon_{N_3}}{\varepsilon_{CH}} \frac{c_{N_3}}{c_{CH}} \ (\text{Eq. 2})$$

The absorption coefficient of the N_3 (ε_{N_3}) and CH band (ε_{CH}) are constant. Because of the large number of benzylic C–H versus the number of incorporated azide moieties (<10%), the concentration of benzylic C–H (c_{CH}) is nearly constant. Thus, the relative IR absorption of the azide moiety (A_{N_3}/A_{CH}) can be approximated to be proportional to a total constant (*C*) and the number of incorporated azide moieties (Eq.3):

$$\frac{A_{N_3}}{A_{CH}} = \frac{\varepsilon_{N_3}}{\varepsilon_{CH}} \frac{c_{N_3}}{c_{CH}} \approx C \times c_{N_3} \ (\text{Eq. 3})$$

The relative IR signals are correlated to the absolute level of functionalization in mol % by a correlation curve obtained from quantitative click reaction and subsequent ^1H NMR analysis (32 scans, t_{delay}=10 sec, 600 MHz at 27 °C) of the 1,3-cycloaddition product. For ^1H NMR analysis, the aromatic protons are referenced to 100 monomer unites (7.37-6.30 ppm, 500 H). The integration of the methoxy protons (4.10-3.50 ppm, 3H) of the formed 1,2,3-

triazol-4-methyl ester moiety is divided by the number of protons (3H) to give an estimation of the level of azide functionalization in mol %.

Here, a representative sample with a relative IR-intensity ratio of azide- to benzylic C–H-strechting band of 1.05 is shown.

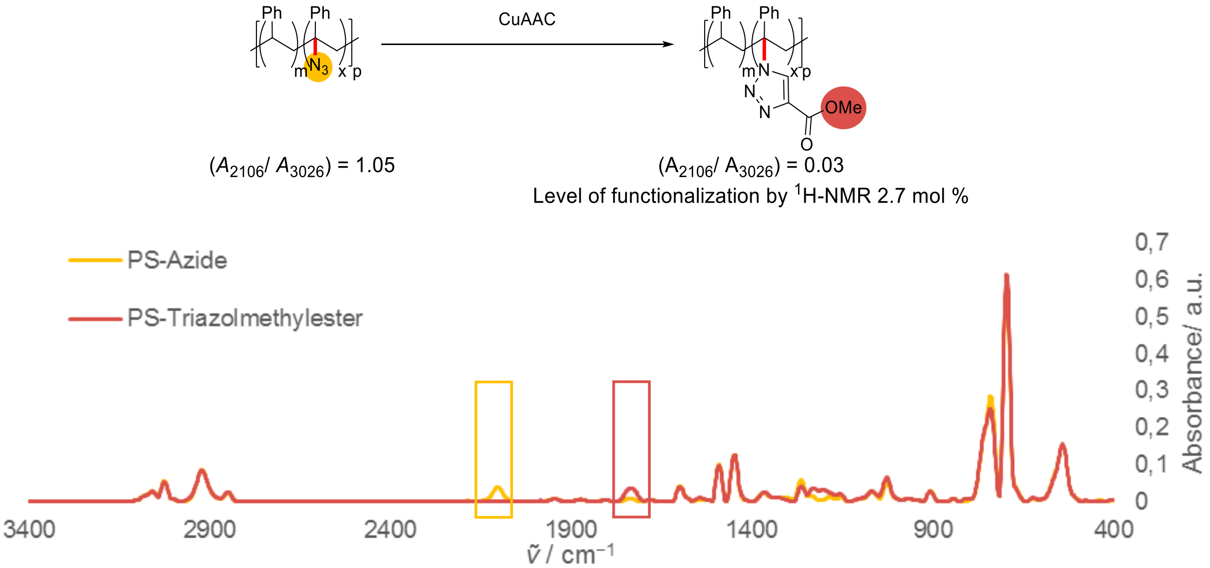


Figure S1. IR spectrum of PS-Azide (yellow) and PS-Triazolmethylester (red) in arbitrary units (a.u.).

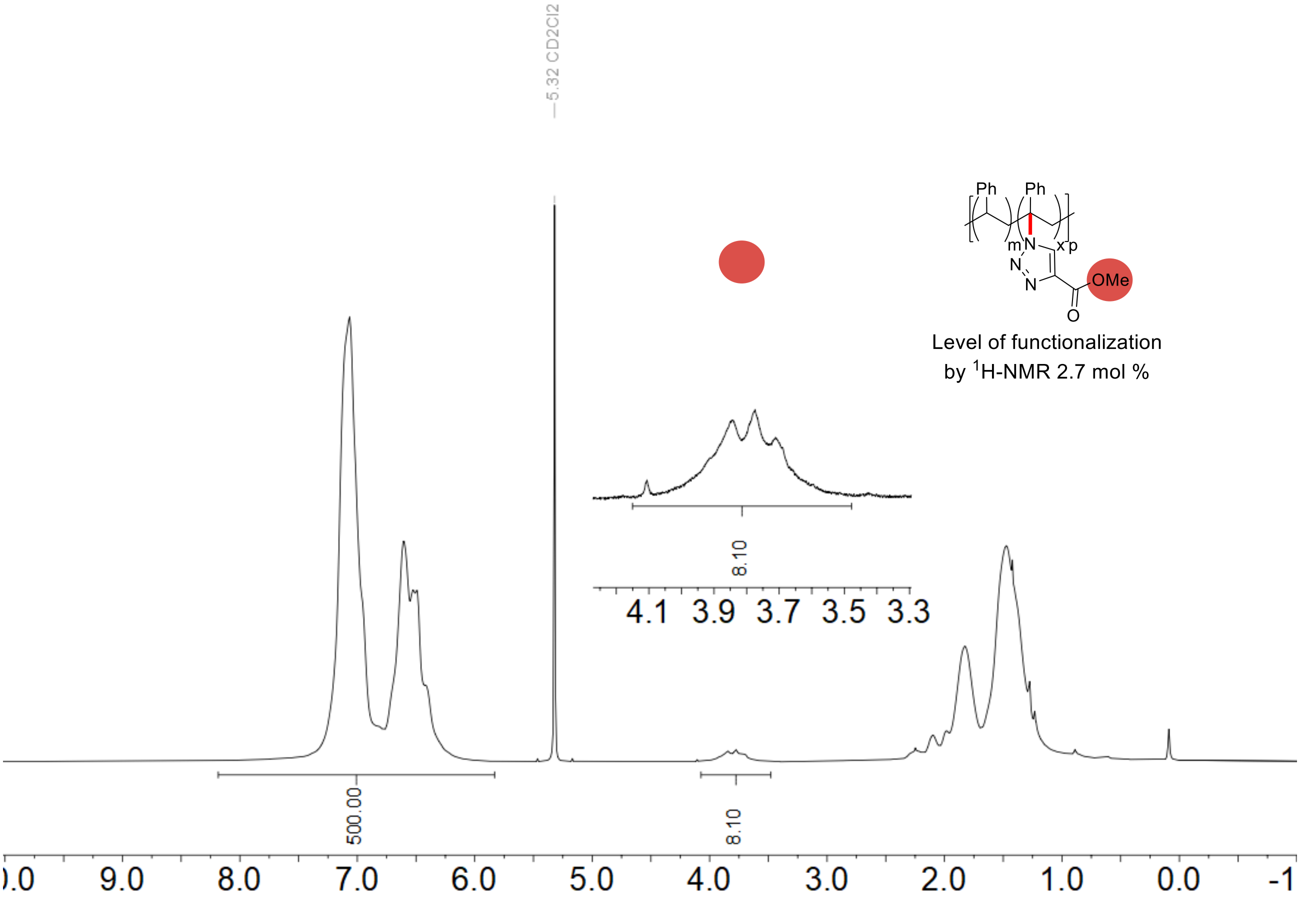


Figure S2. ^{1}H NMR spectrum of PS-Triazolmethyl ester in CD_2Cl_2.

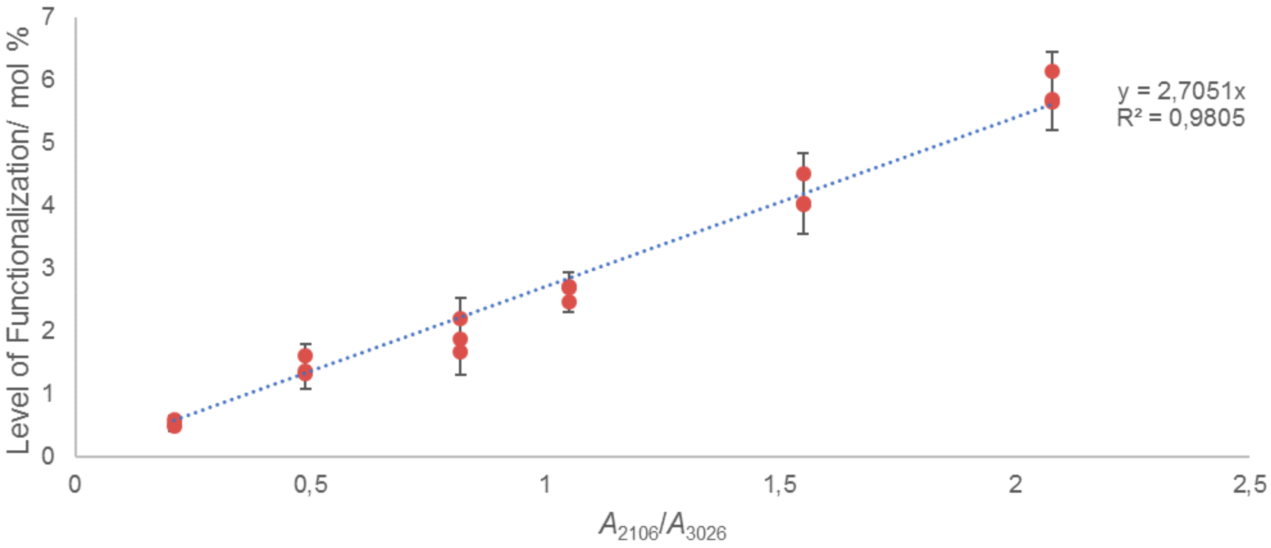
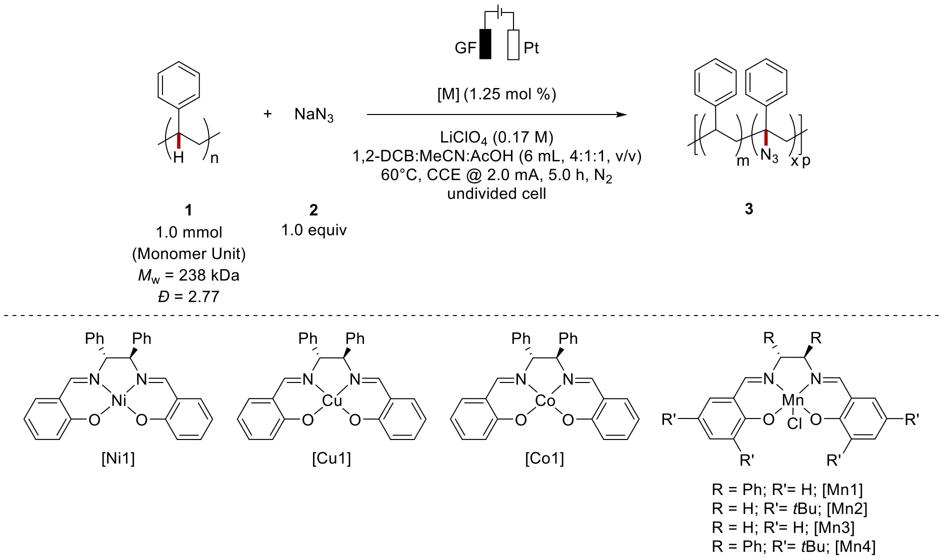


Figure S3. IR-^{1}H NMR correlation curve. Error bars are for confidence level of 95% (*t*-factor = 4.3, N = 3).

3. Optimization Studies

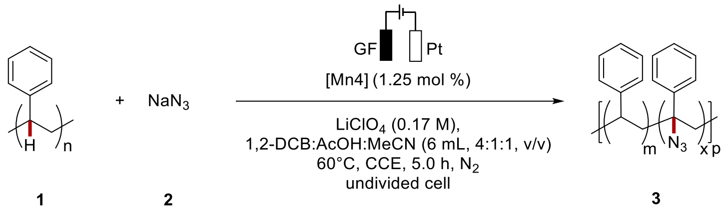
Table S2: Optimization of catalyst.[a]



Entry	[M]	M_w-Retention[b]/ %	$Đ$[b]	IR-Ratio[c]	Level of Functionalization[d]/ mol %
1	[Co1]	77	2.79	0.3	0.8
2	[Ni1]	66	2.88	0.3	0.8
3	[Cu1]	66	3.11	0.4	1.1
4	[Mn1]	48	2.37	0.6	1.6
5	[Mn2]	45	2.41	0.3	0.8
6	[Mn3]	65	2.65	0.7	1.9
7	[Mn4]	69	2.68	0.5	1.4

[a] Reaction conditions: **1** (1.0 mmol monomer unit), **2** (1.0 equiv), [M] (1.25 mol %), $LiClO_4$ (1.0 equiv), 1,2-DCB (4.0 mL), MeCN (1.0 mL), AcOH (1.0 mL) CCE @ 2.0 mA at 60 °C under N_2 for 5.0 h. A stock-solution of **1** in the 1,2-DCB was prepared. [b] The mass average molar mass and polydispersity indices $Đ$ were determined by GPC and are reported against narrow-disperse polystyrene standards using THF as eluent at 30 °C. [c] Relative IR intensity were determined by the ratio of the N_3-Band (2106 cm^{-1}) to the benzylic C–H band (3026 cm^{-1}). [d] The level of functionalization was determined by an IR-^{1}H NMR correlation curve (m = 2.7051 mol %, R^2=0.9942). 1,2-DCB = 1,2-Dichlorobenzene, CCE = Constant Current Electrolysis.

Tabel S3: Optimization of current, catalyst and azide loading.[a]



1
1.0 mmol
(Monomer Unit)
M_w = 238 kDa
$Đ$ = 2.77

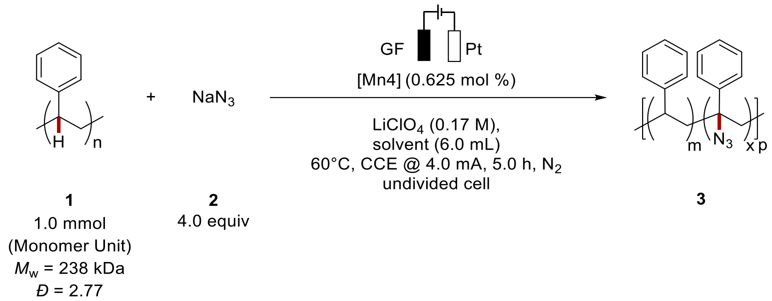
2

3

Entry	CCE @/ mA	[Mn4]/ mol %	NaN$_3$/ equiv	M_w-Retention[b]/ %	$Đ$[b]	IR-Ratio[c]	Level of Functionalization[d]/ mol %
1	1.0	1.25	1.0	89	2.58	0.1	0.3
2	3.0	1.25	1.0	51	2.52	0.8	2.2
3	4.0	1.25	1.0	29	2.33	1.3	3.5
4	4.0	0.00	1.0	64	2.52	0.6	1.6
5	4.0	0.625	1.0	35	2.35	1.4	3.8
6	4.0	2.50	1.0	40	2.35	0.9	2.4
7	4.0	5.00	1.0	74	2.45	0.2	0.5
8[e]	4.0	5.00	1.0	56	2.51	0.4	1.1
9	4.0	0.625	2.0	42	2.35	1.4	3.8
10	4.0	0.625	4.0	56	2.41	1.5	4.1
11[f]	4.0	0.625	6.0	81	2.85	0.6	1.6

[a] Reaction conditions: **1** (1.0 mmol monomer unit), **2** (1.0 equiv), [Mn4] (1.25 mol %), LiClO$_4$ (1.0 equiv), 1,2-DCB (4.0 mL), MeCN (1.0 mL), AcOH (1.0 mL) CCE at 60 °C under N$_2$ for 5.0 h. A stock-solution of **1** in 1,2-DCB was prepared. [b] The mass average molar mass and polydispersity indices $Đ$ were determined by GPC and are reported against narrow-disperse polystyrene standards using THF as eluent at 30 °C. [c] Relative IR intensity were determined by the ratio of the N$_3$-Band (2106 cm^{-1}) to the benzylic C–H band (3026 cm^{-1}). [d] The level of functionalization was determined by an IR-^{1}H NMR correlation curve (m = 2.7051 mol %, R^2=0.9942). [e] CCE for 15 h. [f] Solids did not dissolve completely. 1,2-DCB = 1,2-Dichlorobenzene, CCE = Constant Current Electrolysis.

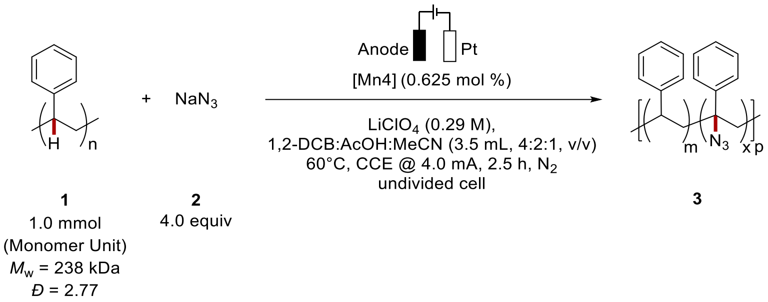
Tabel S4: Optimization of solvent and electrolysis time.[a]



Entry	Solvent	M_w-Retention[b]/ %	$Đ$[b]	IR-Ratio[c]	Level of Functionalization[d]/ mol %
1	1,2-DCB	100	2.81	0.1	0.3
2	1,2-DCB:MeCN (4:2, v/v)	80	2.93	0.4	1.1
3	1,2-DCB:AcOH (4:2, v/v)	44	2.08	1.1	3.0
4[e]	1,2-DCB:AcOH (4:2, v/v)	66	2.85	1.0	2.7
5[f]	DCB:AcOH:MeCN (4:1:1, v/v)	87	2.55	0.5	1.4
6[g]	DCB:AcOH:MeCN (4:1:1, v/v)	68	2.51	0.7	1.9
7[g]	DCB:AcOH:MeCN (3.5 mL, 4:2:1, v/v)	84	2.72	0.7	1.9
8[g,h]	DCB:AcOH:MeCN (4:1:1, v/v)	53	2.39	0.8	2.2

[a] Reaction conditions: **1** (1.0 mmol monomer unit), **2** (4.0 equiv), [Mn4] (1.25 mol %), $LiClO_4$ (1.0 equiv), 1,2-DCB (4.0 mL), MeCN (1.0 mL), AcOH (1.0 mL) CCE @ 4.0 mA at 60 °C under N_2 for 5.0 h. A stock-solution of **1** in 1,2-DCB was prepared. [b] The mass average molar mass and polydispersity indices $Đ$ were determined by GPC and are reported against narrow-disperse polystyrene standards using THF as eluent at 30 °C. [c] Relative IR intensity were determined by the ratio of the N_3-Band (2106 cm^{-1}) to the benzylic C–H band (3026 cm^{-1}). [d] The level of functionalization was determined by an IR-^1H NMR correlation curve (m = 2.7051 mol %, R^2=0.9942). [e] 6.0 equiv of NaN_3. [f] CCE @ 2.0 mA. [g] CCE for 2.5 h. [h] **1** (0.5 mmol) instead of **1** (1.0 mmol). 1,2-DCB = 1,2-Dichlorobenzene, CCE = Constant Current Electrolysis.

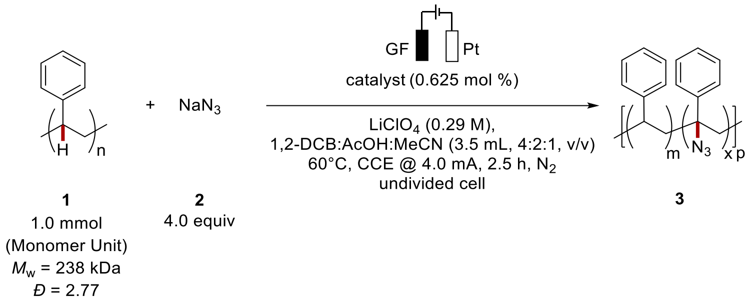
Tabel S5: Optimization of anode material and control reaction.[a]



Entry	Anode	M_w-Retention[b]/ %	$Đ$[b]	IR-Ratio[c]	Level of Functionalization[d]/ mol %
1	RVC	87	2.48	0.3	0.9
2	Graphite	102	2.53	0.1	0.3
3	Graphite rode	102	2.61	0.1	0.3
4	Glassy Carbon	101	2.53	0.2	0.5
5	Boron doped diamond	100	2.54	0.2	0.5
6[e]	Glassy Carbon	81	2.39	0.6	1.5

[a] Reaction conditions: **1** (1.0 mmol monomer unit), **2** (4.0 equiv), [Mn4] (0.625 mol %), $LiClO_4$ (1.0 equiv), 1,2-DCB (2.0 mL), MeCN (0.5 mL), AcOH (1.0 mL) CCE @ 4.0 mA at 60 °C under N_2 for 2.5 h. [b] The mass average molar mass and polydispersity indices *Đ* were determined by GPC and are reported against narrow-disperse polystyrene standards using THF as eluent at 30 °C. [c] Relative IR intensity were determined by the ratio of the N_3-Band (2106 cm^{-1}) to the benzylic C–H band (3026 cm^{-1}). [d] The level of functionalization was determined by an IR-^{1}H NMR correlation curve (m = 2.7051 mol %, R^2=0.9942). [e] CCE for 25 h. 1,2-DCB = 1,2-Dichlorobenzene, CCE = Constant Current Electrolysis.

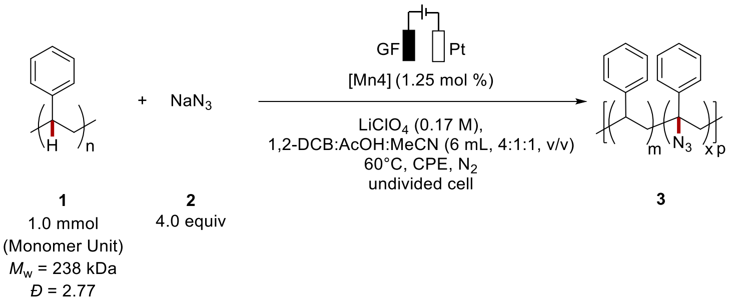
Tabel S6: Control reactions with metal salts as catalyst.[a]



Entry	catalyst	M_w-Retention[b]/ %	$Đ$[b]	IR-Ratio[c]	Level of Functionalization[d]/ mol %
1	$MnCl_2$	51	2.32	1.2	3.2
2	$MnBr_2$	71	2.53	1.1	3.0
3	$FeCl_3$	66	2.50	0.4	1.1
4	$Fe(acac)_3$	91	2.38	0.3	0.9
5	$NiBr_2$	91	2.40	0.4	1.1
6	$Ni(dmg)_2$	91	2.51	0.3	0.7
7	CuI	80	2.51	0.4	1.1
8	$Cu(acac)_2$	74	2.39	0.5	1.3
9	$CoCl_2$	66	2.59	0.2	0.5

[a] Reaction conditions: **1** (1.0 mmol monomer unit), **2** (4.0 equiv), catalyst (0.625 mol %), $LiClO_4$ (1.0 equiv), 1,2-DCB (2.0 mL), MeCN (0.5 mL), AcOH (1.0 mL) CCE @ 4.0 mA at 60 °C under N_2 for 2.5 h. [b] The mass average molar mass and polydispersity indices $Đ$ were determined by GPC and are reported against narrow-disperse polystyrene standards using THF as eluent at 30 °C. [c] Relative IR intensity were determined by the ratio of the N_3-Band (2106 cm^{-1}) to the benzylic C–H band (3026 cm^{-1}). [d] The level of functionalization was determined by an IR-^{1}H NMR correlation curve (m = 2.7051 mol %, R^2=0.9942). 1,2-DCB = 1,2-Dichlorobenzene, CCE = Constant Current Electrolysis.

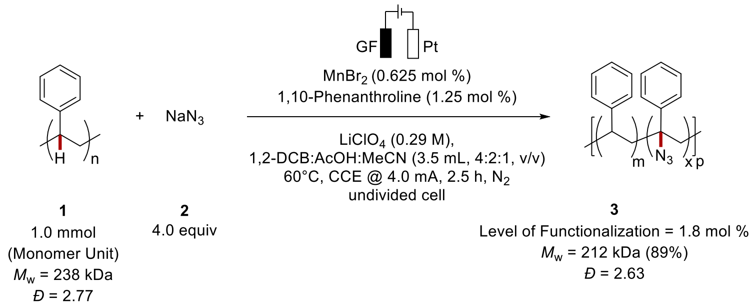
Tabel S7: Optimization on constant potential electrolysis.[a]



Entry	Deviation	M_w-Retention[b]/ %	Đ[b]	IR-Ratio[c]	Level of Functionalization[d]/ mol %
1	CPE @ 1.0 V vs Ag, 0.4 F/mol	89	2.74	0.3	0.8
2	CPE @ 0.8 V vs Ag, 0.4 F/mol	79	2.61	0.5	1.4
3	CPE @ 0.6 V vs Ag, 0.4 F/mol	87	2.59	0.2	0.5
4	CPE @ 1.0 V, 2.0 F/mol	39	2.55	2.1	5.7
5	CPE @ 0.8 V vs Ag, 2.0 F/mol	20	2.19	2.9	7.8

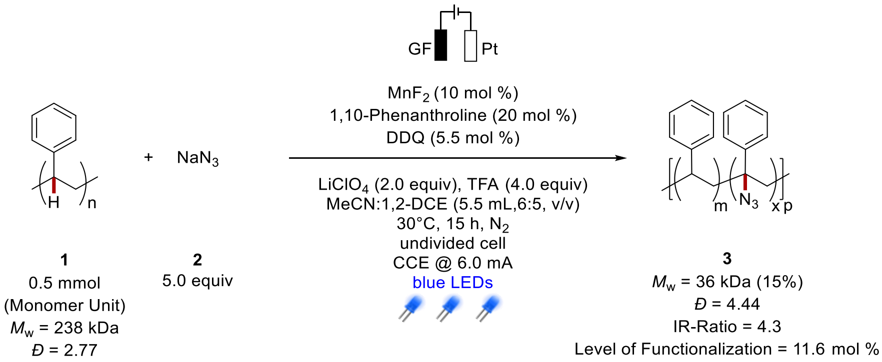
[a] Reaction conditions: **1** (1.0 mmol monomer unit), **2** (4.0 equiv), [Mn4] (1.25 mol %), $LiClO_4$ (0.17 M), 1,2-DCB (4.0 mL), MeCN (1.0 mL), AcOH (1.0 mL), CPE @ 1.0 V at 60 °C under N_2 for 0.4 F/mol. [b] The mass average molar mass and polydispersity indices Đ were determined by GPC and are reported against narrow-disperse polystyrene standards using THF as eluent at 30 °C. [c] Relative IR intensity were determined by the ratio of the N_3-Band (2106 cm^{-1}) to the benzylic C–H band (3026 cm^{-1}). [d] The level of functionalization was determined by an IR-^{1}H NMR correlation curve (m = 2.7051 mol %, R^2=0.9942). 1,2-DCB = 1,2-Dichlorobenzene, CPE = Constant Potential Electrolysis.

Alternative Catalytic System



Alternative catalyst precursor system. Reaction conditions: 1 (1.0 mmol monomer unit), 2 (4.0 equiv), $MnBr_2$ (0.625 mol %), 1,10-phenanthroline (1.25 mol %), $LiClO_4$ (1.0 equiv), 1,2-DCB (2.0 mL), MeCN (0.5 mL), AcOH (1.0 mL) CCE @ 4.0 mA at 60 °C under N_2 for 2.5 h. The mass average molar mass and polydispersity indices Đ were determined by GPC and are reported against narrow-disperse polystyrene standards using THF as eluent at 30 °C. The level of functionalization was determined by an IR-^{1}H NMR correlation curve (m = 2.7051 mol %, R^2=0.9942).

PS-Azidation using a Photelectrocatalytic Conditions



Adapted from the previous report of the Aiwen Lei Group,[5] a schlenk tube was charged with NaN_3 (162.5 mg, 5.0 equiv), MnF_2 (4.6 mg, 10 mol %), 1,10-Phenanthroline (18.6 mg, 20 mol %), DDQ (6.2 mg, 5.5 mol %), $LiClO_4$ (106.4 mg, 2.0 equiv) and was evacuacted and backfilled with N_2 three times. A stock solution of polystyrene (52 mg, 0.5 mmol per repeating unit, M_w = 238 kDa, $Đ$ = 2.77) in 1,2-DCE (2.5 mL) was prepared and added under N_2. Then, MeCN (3.0 mL) and TFA (154 µL, 4.0 equiv) were added and the electrodes equipped in a N_2-Flow. The reaction was irradiated with blue LEDs and electrolyzed @ 6.0 mA for 15 h at 30 °C. After the electrolysis, the reaction mixture was filtered over a plug of celite and was poured in MeOH (50 mL). The graphite felt electrode was extracted with DCM (3 x 3 mL), which was then filtered and added to the beaker containing MeOH. The solids were collected over a glass-sintered funnel, washed with methanol (20 mL), water (2 x 5 mL) and methanol (20 mL) successively and dried in vacuo at room temperature for 12 h, giving a white solid (45.4 mg, M_w = 36 kDa, $Đ$ = 4.44, 11.6 mol % N_3 Functionalization). The level of functionalization was determined by an IR-^{1}H NMR correlation curve as 11.6 mol %.

4. Electrochemical Setup

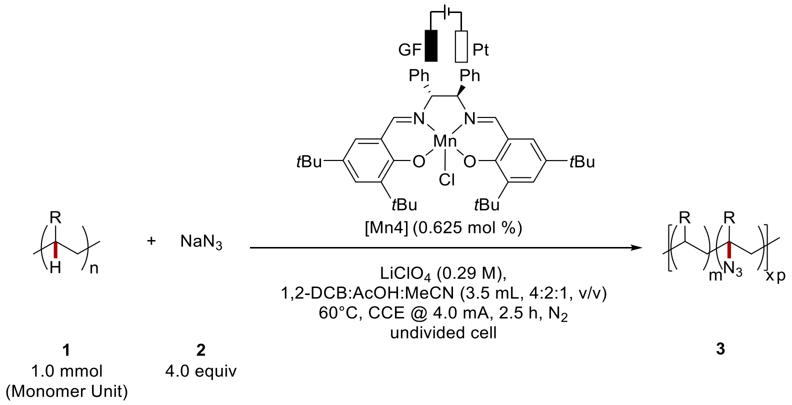
Figure S4. Picture of the electrochemical cell, stirring bar and teflon cap with graphite felt and platinum electrode.

5. General Procedure

General procedure 1 (GP1) for manganese-catalyzed electrooxidative C–H azidation of polymers

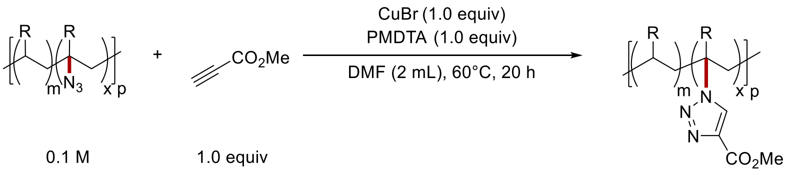
A stock solution of the [Mn4] (23 mg) in 1,2-DCB (5.0 mL) was prepared.

A Schlenk tube charged with polymer (1.0 mmol per repeating unit), sodium azide (260 mg, 4.0 equiv), $LiClO_4$ (106 mg, 1.0 equiv) was evacuated and backfilled with nitrogen three times. Then, 1.0 mL of the stock solution of [Mn4] and 1,2-DCB (1.0 mL) were added. The polymer was dissolved at 60 °C and 750 rpm under N_2 (ca. 1.0 h). MeCN (0.5 mL) and AcOH (1.0 mL) were added under continues stirring at 750 rpm. After dissolving the remaining components, the electrodes were equipped in a strong N_2 flow and the cap sealed with parafilm stripes. The electrolysis was initiated at the Methrohm Autolab at 60 °C for 2.5 h at 4.0 mA of constant current and 750 rpm. After the electrolysis, the reaction mixture was filtered over a plug of celite and precipitated dropwise in vigorously stirring MeOH (50 mL). The graphite felt electrode was extracted with DCM (3 x 3 mL), which was then filtered and added to the beaker containing MeOH. The supernatant was decanted, and the remaining solids were stirred in MeOH (20 mL) for 10 min. The solids were collected over a glass-sintered funnel, washed with methanol (20 mL), water (2 x 5 mL) and methanol (20 mL) successively. The solids were redissolved in DCM (2 mL) and precipitated in stirring MeOH (20 mL). After collection and washing with MeOH (20 mL), the solids were dried *in vacuo* at room temperature for 12 h.



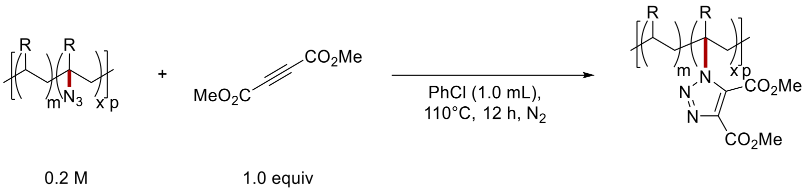
General procedure 2 (GP2) for copper-catalyzed 1,3-dipolar cycloaddition on polymer-azide

In a Schlenk tube the azidated polymer (0.20 mmol per repeating unit) and CuBr (29.0 mg, 0.20 mmol, 1.0 equiv) were evacuated and backfilled with N_2 three times. Then, PMDTA (34.7 mg, 0.20 mmol, 1.0 equiv), methyl propiolate (16.8 mg, 0.20 mmol, 1.0 equiv) and DMF (2.0 mL) were added and stirred at 60 °C for 20 h. After the reaction cooled down, the crude mixture was diluted with THF (8.0 mL) and washed with NH_4Cl (3 x 10 mL). The combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated by rotary evaporation. The product was precipitated from MeOH (10 mL) and collected over a sintered glass-funnel, washed with MeOH (2 x 10 mL) and dried *in vacuo* for 12 h.



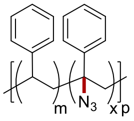
General procedure 3 (GP3) for thermal 1,3-dipolar cycloaddition of polymer-azide

According to a previous report,[6] a Schlenk tube was charged with the azidated polymer (0.20 mmol per repeating unit) and was evacuated and backfilled with N_2 three times. Then, degassed chlorobenzene (1.0 mL) was added, and the material was dissolved at 110 °C. After adding dimethyl acetylenedicarboxylate (28.4 mg, 0.20 mmol, 1.0 equiv), the reaction was stirred at 110 °C for 12 h. After the reaction cooled down, the crude was precipitated in acetone (10 mL) and collected by centrifugation. The obtained material was dried *in vacuo* for 12 h.



6. Characterization of azidated Polymers

Polystyrene-Azide **3**



3

The general procedure **GP1** was followed using polystyrene (104 mg, 1.0 mmol, 1.0 equiv, M_w = 238 kDa, $Đ$ = 2.77, Thermo Scientific, atactic, LOT # WO2G019). Precipitation from MeOH yielded **3** (77.2 mg, M_w = 199 kDa, $Đ$ = 2.72, 1.9 mol % N_3-Functionalization) as a white solid. Upon purification the percent of azide moieties were determined by correlating the relative IR intensity of the N_3- and CH-band with level of functionalization of the 1,3-cycloaddition product from section **2**. For this purpose, the area in the IR spectrum from $\tilde{\nu}$ = 3047 cm^{-1} – 2995 cm^{-1} (benzylic C–H band) and from $\tilde{\nu}$ = 2153 cm^{-1} – 2040 cm^{-1} (azide band) were integrated. The level of functionalization obtained by the IR-^{1}H NMR correlation was confirmed by ^{1}H NMR analysis of the 1,3-cycloaddition product of **3** with methyl propiolate (1.8 mol %) and elemental analysis (2.1 mol % for 1st run). The following ^{13}C NMR data was collected using at least 50 mg of **3** from the 1st run. The observed ^{13}C NMR signals are in good agreement with reported small molecule model compound[7] and support the proposed structural assignment. For elemental analysis the sample was dissolved in dichloromethane and reprecipitated in MeOH and dried *in vacuo* for 12 h.

1st run: 77.2 mg, M_w = 199 kDa, $Đ$ = 2.72, 1.9 mol % N_3-Functionalization
2nd run: 83.5 mg, M_w = 201 kDa, $Đ$ = 2.51, 1.9 mol % N_3-Functionalization
3rd run: 84.7 mg, M_w = 190 kDa, $Đ$ = 2.49, 2.1 mol % N_3-Functionalization

^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.37–6.94 (br, 300H), 6.87–6.30 (br, 200H), 2.45–1.70 (br, 100H), 1.69–1.22 (br, 200H).

^{13}C NMR (126 MHz, CD_2Cl_2) δ 146.5–145.4 (C_q), 140.8 (C_q), 128.5–127.2 (4 x CH), 126.6–125.8 (2 x CH), 70.5 (C_q), 46.8–41.0 (2 x CH_2), 40.9–31.9 (CH).

IR (ATR): $\tilde{\nu}$ = 3065, 3026, 2922, 2851, 2106 (azide N_3 stretching), 1945, 1875, 1806, 1744, 1599, 1493, 1450, 1026, 753, 698, 542 cm^{-1}.

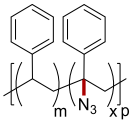
GPC (THF): Parent: M_w = 238 kDa, $Đ$ = 2.77; Functionalized: M_w = 199 kDa, $Đ$ = 2.72.

DSC (°C, 10 °C/min): Parent: T_g = 98.7; Functionalized: T_g = 107.4.

TGA (°C, 20 °C/min): Parent: T_{deg} = 403.8; Functionalized: T_{deg} = 362.8.

Elemental Analysis: calcd. for $C_8H_{8-x}N_{3x}$ with x = 0.021 C 91.50 H 7.66 N 0.84, found C 90.61 H 7.63 N 0.84.

Polystyrene-Azide **4**



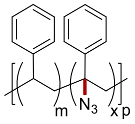
4

The general procedure **GP1** was followed using polystyrene (104 mg, 1.0 mmol, 1.0 equiv, M_w = 16.7 kDa, $Đ$ = 1.04). Precipitation from MeOH yielded **4** (74.7 mg, M_w = 16.6 kDa, $Đ$ = 1.07, 1.7 mol % N_3-Functionalization) as a white solid. Precipitation of **4** after 5.0 h CCE gave an off-white solid (42.5 mg, M_w = 16.5 kDa, $Đ$ = 1.14, 6.7 mol % N_3-Functionalization). Upon purification the percent of azide moieties were determined by correlating the relative IR intensity of the N_3- and CH-band with level of functionalization of the 1,3-cycloaddition product from section **2**. For this purpose, the area in the IR spectrum from $\tilde{\nu}$ = 3047 cm^{-1} – 2995 cm^{-1} (benzylic C–H band) and from $\tilde{\nu}$ = 2153 cm^{-1} – 2040 cm^{-1} (azide band) were integrated. The following ^{13}C NMR data was collected using at least 50 mg of **4** (CEE = 2.5 h) from the 1st run.

1st run: (CCE = 2.5 h): 74.7 mg, M_w = 16.6 kDa, $Đ$ = 1.07, 1.7 mol % N_3-Functionalization
(CCE = 5.0 h): 42.5 mg, M_w = 16.5 kDa, $Đ$ = 1.14, 6.7 mol % N_3-Functionalization
2nd run: (CCE = 2.5 h): 84.0 mg, M_w = 16.5 kDa, $Đ$ = 1.09, 2.2 mol % N_3-Functionalization
(CCE = 5.0 h): 80.1 mg, M_w = 16.7 kDa, $Đ$ = 1.15, 6.9 mol % N_3-Functionalization
3rd run: (CCE = 2.5 h): 82.6 mg, M_w = 16.9 kDa, $Đ$ = 1.10, 2.4 mol % N_3-Functionalization
(CCE = 5.0 h): 83.2 mg, M_w = 16.7 kDa, $Đ$ = 1.11, 6.8 mol % N_3-Functionalization

^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.37–6.94 (br, 300H), 6.87–6.30 (br, 200H), 2.45–1.70 (br, 100H), 1.69–1.22 (br, 200H).
^{13}C NMR (126 MHz, CD_2Cl_2) δ 146.5–145.4 (C_q), 140.9 (C_q), 128.5–127.2 (4 x CH), 126.6–125.8 (2 x CH), 70.6 (C_q), 46.8–41.0 (2 x CH_2), 40.9–31.9 (CH).
IR (ATR): $\tilde{\nu}$ = 3065, 3026, 2922, 2851, 2106 (azide N_3 stretching), 1945, 1875, 1806, 1744, 1599, 1493, 1450, 1026, 753, 698, 542 cm^{-1}.
DSC (°C, 10 °C/min): Parent: T_g = 101.3; Functionalized (CCE = 2.5 h): T_g = 98.6.
Functionalized (CCE = 5.0 h): T_g = 104.1.
TGA (°C, 20 °C/min): Parent: T_{deg} = 410.2; Functionalized (CCE = 2.5 h): T_{deg} = 382.2.
Functionalized (CCE = 5.0 h): T_{deg} = 339.7.
GPC (THF): Parent: M_w = 16.7 kDa, $Đ$ = 1.04; Functionalized (CCE = 2.5 h): M_w = 16.9 kDa, $Đ$ = 1.10.
Functionalized (CCE = 5.0 h): M_w = 16.5 kDa, $Đ$ = 1.14.

Polystyrene-Azide **5**



5

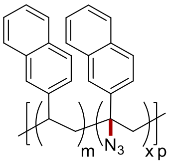
The general procedure **GP1** was followed using polystyrene (104 mg, 1.0 mmol, 1.0 equiv, M_w = 65.8 kDa, $Đ$ = 1.85). Precipitation from MeOH yielded **5** (68.7 mg, M_w = 61.4 kDa, $Đ$ = 1.83, 1.7 mol % N_3-Functionalization) as a white solid. Upon purification the percent of azide moieties were determined by correlating the relative IR intensity of the N_3- and CH-band with level of functionalization of the 1,3-cycloaddition product from section **2**. For this purpose, the area in the IR spectrum from $\tilde{\nu}$ = 3047 cm^{-1} – 2995 cm^{-1} (benzylic C–H band) and from $\tilde{\nu}$ = 2153 cm^{-1} – 2040 cm^{-1} (azide band) were integrated. The level of functionalization obtained by the IR-^{1}H NMR correlation was confirmed by elemental analysis of **5** (2.1 mol % for 1st run). The following ^{13}C NMR data was collected using at least 50 mg of **5** from the 1st run.

1st run: 68.7 mg, M_w = 61.4 kDa, $Đ$ = 1.83, 1.7 mol % N_3-Functionalization
2nd run: 82.3 mg, M_w = 60.4 kDa, $Đ$ = 1.99, 1.6 mol % N_3-Functionalization
3rd run: 92.5mg, M_w = 65.1 kDa, $Đ$ = 1.89, 2.3 mol % N_3-Functionalization

^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.37–6.94 (br, 300H), 6.87–6.30 (br, 200H), 2.45–1.70 (br, 100H), 1.69–1.22 (br, 200H).

^{13}C NMR (126 MHz, CD_2Cl_2) δ 146.2–145.4 (C_q), 140.9 (C_q), 128.5–127.2 (4 x CH), 126.6–125.8 (2 x CH), 70.7 (C_q), 48.6–41.4 (2 x CH_2), 41.3–39.1 (CH).
IR (ATR): $\tilde{\nu}$ = 3065, 3026, 2922, 2851, 2106 (azide N_3 stretching), 1945, 1875, 1806, 1744, 1599, 1493, 1450, 1026, 753, 698, 542 cm^{-1}.
DSC (°C, 10 °C/min): Parent: T_g = 105.9; Functionalized: T_g = 104.3.
TGA (°C, 20 °C/min): Parent: T_{deg} = 409.8; Functionalized: T_{deg} = 398.4.
GPC (THF): Parent: M_w = 65.8 kDa, $Đ$ = 1.85; Functionalized: M_w = 61.4 kDa, $Đ$ = 1.83.
Elemental Analysis: calcd. for $C_8H_{8-x}N_{3x}$ with x = 0.021 C 91.50 H 7.66 N 0.84, found C 90.82 H 7.65 N 0.84.

Poly(2-vinylnaphatlene)-Azide **6**

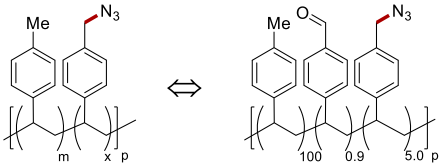


6

The general procedure **GP1** was followed using poly(2-vinylnaphthalene) (156 mg, 1.0 mmol, 1.0 equiv, M_w = 44 kDa, $Đ$ = 1.08, Sigma Aldrich). Precipitation from MeOH yielded azide functionalized polymer **6** (145 mg, M_w = 41 kDa, $Đ$ = 1.09, 2.6 mol % N_3-Functionalization) as an off-white solid. To determine the level of functionalization, **6** was reacted with methyl propiolate according to **GP2**. Upon purification the percent of azide moieties were determined by integration of the ^{1}H NMR. The aromatic signals δ = 8.17–5.70 ppm were integrated to a total of 700. The protons of the methyl ester moiety of the 1,3-cycloaddition product that appear at 3.94–3.14 ppm are used to determine the mol % azide per repeat unit as demonstrated in section **2**. This level of functionalization is in agreement with the level of functionalization determined by elemental analysis. The following NMR data was gathered using 50 mg of **6**.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.17–5.70 (br, 700H), 3.40–1.74 (br, 100H), 1.74–0.37 (br, 200H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 144.3–141.6 (2 x C_q), 133.3–132.8 (2 x C_q), 132.4–131.6 (2 x C_q), 128.5–124.5 (14 x CH), 70.2 (C_q), 46.2–41.3 (2 x CH_2), 41.2–39.7 (CH).
IR (ATR): $\tilde{\nu}$ = 3045, 3008, 2918, 2844, 2095 (azide N_3 stretching), 1954, 1918, 1633, 1601, 1510, 1438, 1382, 1271, 1118, 1013, 956, 897, 855, 818, 741, 707, 666, 626, 474 cm^{-1}.
DSC (°C, 10 °C/min): Parent: T_g = 146.8; Functionalized: T_g = 151.1.
TGA (°C, 20 °C/min): Parent: T_{deg} = 422.3; Functionalized: T_{deg} = 400.4.
GPC (THF): Parent: M_w = 44 kDa, $Đ$ = 1.08; Functionalized: M_w = 41 kDa, $Đ$ = 1.09.
Elemental Analysis: calcd. for $C_{12}H_{10-x}N_{3x}$ with x = 0.031 C 92.69 H 6.47 N 0.84, found C 90.20 H 6.13 N 0.84.

Poly(4-methylstyrene)-Azide **7**



7

The general procedure **GP1** was followed using poly(4-methylstyrene) (118 mg, 1.0 mmol, 1.0 equiv, M_w = 120 kDa, $Đ$ = 3.08, Sigma Aldrich, LOT # MKCM8487). Precipitation from MeOH yielded **7** (93.1 mg, M_w = 180 kDa, $Đ$ = 4.69, 5.0 mol % N_3-Functionalization) as a white solid. To determine the level of functionalization, **7** was reacted with methyl propiolate according to **GP2**. Upon purification the percent of azide moieties were determined by integration of the ^{1}H NMR. The aromatic signals δ = 7.20–5.95 were integrated to a total of 400. The protons of the methyl ester moiety of the 1,3-cycloaddition product that appear at δ = 4.33–3.62 ppm are used to determine the mol % azide per repeat unit as demonstrated in section **2**. This level of functionalization is in agreement with the level of functionalization determined by ^{1}H NMR analysis of **7** (4.8 mol %, CH_2 at δ = 4.47–4.00) and elemental analysis (5.0 mol %).

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.99–9.73 (br, 0.51H, CHO), 7.96–7.86 (br, 0.81H, CH), 7.60–7.50 (br, 1.12H, CH), 7.44–7.34 (br, 1.25, CH), 7.44–7.34 (br, 200H), 7.17–5.93 (br, 200H), 4.47–4.00 (br, 9.60H, CH_2), 3.13–2.05 (br, 300H), 2.10–1.66 (br, 100H), 1.61–1.16 (br, 200H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 192.1 (CHO), 143.9–141.9 (3 x C_q), 135.4–134.3 (2 x C_q), 132.4 (C_q), 129.4–128.3 (3 x CH), 128.2–126.9 (3 x CH), 54.8 (CH_2), 47.0–41.0 (3 x CH_2), 40.9–39.4 (3 x CH), 21.7–20.9 (CH_3).

IR (ATR): $\tilde{\nu}$ = 3096, 3053, 3023, 2924, 2849, 2097 (azide N_3 stretching), 1906, 1800, 1712, 1610, 1517, 1450, 1371, 1270, 1197, 1115, 1028, 817, 729, 548 cm^{-1}.

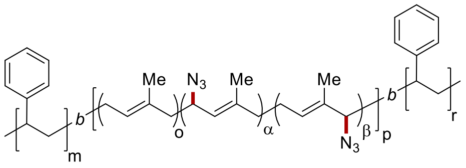
GPC (THF): Parent: M_w = 120 kDa, $Đ$ = 3.08; Functionalized: M_w = 180 kDa, $Đ$ = 4.69.

DSC (°C, 10 °C/min): Parent: T_g = 105.0; Functionalized: T_g = 112.9.

TGA (°C, 20 °C/min): Parent: T_{deg} = 408.9; Functionalized: T_{deg} = 411.8.

Elemental Analysis: calcd. for $C_9H_{10-x}N_{3x}$ with x = 0.050 C 90.09 H 8.37 N 1.75, found C 89.21 H 8.20 N 1.75.

Polystyrene-*b*-isoprene-*b*-polystyrene-Azide **8**



8

The general procedure **GP1** was followed using polystyrene-*b*-polyisoprene-*b*-polystyrene (76 mg, 1.0 mmol, 1.0 equiv, M_w = 169 kDa, $Đ$ = 1.46, Sigma Aldrich, LOT # MKCP3021). Precipitation from MeOH yielded **8** (64 mg, M_w = 168 kDa, $Đ$ = 2.59, 14.0 mol % N_3-Functionalization) as a white solid. Upon purification the percent of azide moieties were determined by integration of the ^{1}H NMR. The aromatic signals δ = 7.38–6.22 were integrated to a total of 500. The protons of the methyl ester moiety of the 1,3-cycloadition product that appear at 3.80–3.57 ppm is used to determine the mol % azide per repeat unit. To account the ratio of the styrene to isoprene ratio, the result was multiplied with the ratio of the styrene block (21 mol %) to obtain an estimation of azide moieties per 100 repeating unit of 14.0 mol %. This level of functionalization was determined by elemental analysis as 10.5 mol %. The ratio of α and β moiety was determined by the corresponding proton signal at 4.44–4.17 and 4.00–3.75 ppm, respectively and equal 1.0:1.5. The following NMR data was acquired using 50 mg of sample. The azide related carbon signal could not be detected for **8** due to overlapping signals. However, by comparison of the HSQC of the parent polymer and **8**, the assignment can be done and further supported by the HSQC analysis of the 1,3-cycloaddition product **18**. For elemental analysis the sample was dissolved in tetrahydrofurane and reprecipitated in MeOH and dried *in vacuo* for 12 h.

The following assignment of the bulk poly(isobutene) NMR signals were conducted according to a previous report by Rozentsvet, Khachaturov and Ivanova.[8] The polyisoprene (PIP) block consists mainly of 1,4-addition repeating units (≈88%). For clarity, 1,2-, 3,4-, 4,4- and 1,1-addition units were omitted in the structure representation.

^{1}H NMR (600 MHz, THF-d_8) δ 7.35–6.82 (br, 300H), 6.81–6.20 (br, 200H), 5.69–5.57 (br, 8.50H, CH), 5.56–5.38 (br, 10.72H, CH), 5.14 (br, 376 H), 4.81–4.69 (d, J = 16.2 Hz, 37H) 4.68–4.61 (d, J = 17.0 Hz, 29 H), 4.44–4.17 (br, 7.38, CH), 4.00–3.75 (br, 10.75, CH), 2.62–2.32 (br, 340H), 2.34–1.79 (br, 1828 H), 1.76–1.24 (br, 2158H).

^{13}C NMR (126 MHz, THF-d_8) δ 148.0–145.8 (C_q), 137.0–135.2 (C_q), 131.0–129.5 (CH), 130.0–127.7 (CH), 127.3–125.7 (CH), 125.6–124.0 (CH), 112.8–111.0 (CH_2), 72.6–70.6 (CH), 60.1–58.2 (CH), 49.9–47.8 (CH), 47.5–42.3 (CH_2), 42.2–41.4 (CH), 41.3–40.1 (CH_2), 39.1–37.8 (CH_2), 33.7–32.7 (CH_2), 32.6–31.5 (CH_2), 31.4–30.1 (CH_2), 30.0–28.8 (CH_2), 28.7–26.8 (CH_2), 24.3–23.1 (CH_3 and CH_2), 19.7–17.9 (CH_3), 17.3–15.4 (CH_3). Three C_q are missing due to signal overlap.

IR (ATR): $\tilde{\nu}$ = 2967, 2918, 2850, 2093 (azide N_3 stretching), 1448, 1369, 953, 697 cm^{-1}

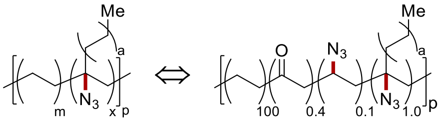
DSC : No glass transition was observed the experimental accessible temperature range.

TGA (°C, 20 °C/min): Parent: T_{deg} = 384.7; Functionalized: T_{deg} = 358.7.

GPC (THF): Parent: M_w = 169 kDa, $Đ$ = 1.46; Functionalized: M_w = 168 kDa, $Đ$ = 2.59.

Elemental Analysis: calcd. for $C_{8x+5y}H_{8-z}N_{3z}$ with x = 0.21, y = 0.79, z = 0.10 C 84.36 H 9.94 N 5.51, found C 83.10 H 9.95 N 5.53.

Polyethylene-Azide **9**



9

The general procedure **GP1** was followed at 80 °C using polyethylene (28 mg, 1.0 mmol, 1.0 equiv, LD-PE, 500 micron, Alfa Aesar, LOT # 10224422, branching = 26 Me/1000C). Precipitation from MeOH (30 mL) and collection by centrifugation yielded **9** (17.6 mg, 1.0 mol % N_3-Functionalization, 25 Me/1000C) as a pale brown solid. The proton adjacent to the azide moiety that appear at 3.20 ppm was used to determine the mol % of the secondary C(sp^3)–H azidation (0.1 mol %) per repeat unit as demonstrated in section **2**. However, the total level of functionalization determined by elemental analysis (1.0 mol %) and the ^{1}H NMR analysis of the 1,3-cycloaddition product with dimethyl acetylenedicarboxylate (1.1 mol %) indicate that the C(sp^3)–H azidation mainly took place on the tertiary C–H of the polymer branches. The ration 3° to 2° azidation equals 10:1. The level of ketone functionalization equals 0.4 mol %. The selectivity for azidation versus oxygenation equals to 2.8:1.0. The branching was determined by ^{1}H NMR analysis as 25 Me/1000C.[9] For elemental analysis the sample was dissolved in tetrachloroethane at 80 °C and reprecipitated in MeOH and dried *in vacuo* for 48 h at 60 °C.

^{1}H NMR (600 MHz, $C_2D_2Cl_4$, 75 °C) δ 3.20 (q, J = 6.4 Hz, 0.13H, CH), 2.33 (t, J = 7.0 Hz, 1.65H, CH_2), 2.20–1.01 (br, 400H), 1.00–0.39 (br, 16H).

^{13}C NMR (126 MHz, $C_2D_2Cl_4$, 75 °C) δ 67.2 (C_q), 63.5 (CH), 43.4–41.8 (2 x CH_2), 35.2–21.4 (4 x CH_2), 14.6–10.0 (CH_3). One C_q is missing due to low signal to noise ratio.

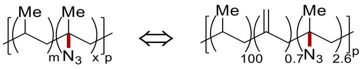
IR (ATR): $\tilde{\nu}$ = 2923, 2846, 2098 (azide N_3 stretching), 1718, 1465, 1370, 1253, 1106, 1033, 812, 723 cm^{-1}.

DSC (°C, 10 °C/min): Parent: T_m = 109.9; Functionalized: T_m = 109.7.

TGA (°C, 20 °C/min): Parent: T_{deg} = 459.5; Functionalized: T_{deg} = 430.6.

Elemental Analysis: calcd. for $C_2H_{4-x}N_{3x}$ with x = 0.01 C 84.39 H 14.13 N 1.48, found C 83.06 H 13.64 N 1.43.

Polypropylene-Azide **10**



10

The general procedure **GP1** was followed at 120 °C using as stock solution of polypropylene in 1,2-DCB (1.0 M, 1.0 mL, 1.0 mmol, 1.0 equiv; M_w = 12 kDa, $Đ$ = 2.40, Sigma Aldrich, isotatic, LOT # MKCM0168). Precipitation from MeOH yielded **10** (17.3 mg, 2.6 mol % N_3-Functionalization) as a brown solid. Upon purification the percent of azide moieties were determined by integration of the ^{1}H NMR. The aliphatic signals δ = 1.66–0.81 ppm were integrated to a total of 600. The protons of the CH_3 of methyl ester moieties (in total 6 H) of the 1,3-cycloaddition product that appear at 4.59−3.95 ppm are used to determine the mol % azide per repeat unit as demonstrated in section **2**. The level of functionalization determined by ^{1}H NMR analysis of the 1,3-cycloaddition product (2.6 mol %) was confirmed by elemental analysis (2.1 mol %). The protons δ = 4.83−4.70 correspond to internal vinylidene moieties (0.7 mol %).[6] For elemental analysis the sample was dissolved in tetrachloroethane at 80 °C and reprecipitated in MeOH and dried *in vacuo* for 48 h at 60 °C.

^{1}H NMR (600 MHz, $C_2D_2Cl_4$, 75°C) δ 4.83−4.70 (s, 1.32H, CH_2) 1.66−1.54 (br, 100H), 1.30−1.19 (br, 100 H), 0.95−0.81 (br, 400H).

^{13}C NMR (126 MHz, $C_2D_2Cl_4$, 75°C) δ 111.8 (CH_2), 65.2−64.2 (C_q), 65.2−64.2 (C_q), 47.1−45.3 (2 x CH_2), 30.6−28.3 (CH), 24.4−20.3 (3 x CH_3). One C_q is missing due to low signal to noise ratio.

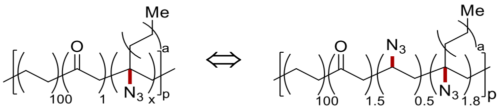
IR (ATR): $\tilde{\nu}$ = 2951, 2916, 2874, 2834, 2093 (azide N_3 stretching), 1452, 1371, 1252, 1153, 968, 798 cm^{-1}.

DSC (°C, 10 °C/min): Parent: T_m = 147.0; Functionalized: T_m = 143.8.

TGA (°C, 20 °C/min): Parent: T_{deg} = 423.0; Functionalized: T_{deg} = 415.5.

Elemental Analysis: calcd. for $C_3H_{6-x}N_x$ with x = 0.021 C 83.86 H 14.02 N 2.12, found C 81.71 H 13.22 N 2.10.

Polyethylene-Azide **11**



11

The general procedure **GP1** was followed at 80 °C using polyethylene (28.1 mg, 1.0 mmol; M_w = 4 kDa, $Đ$ = 2.35, Sigma Aldrich, LD-PE, LOT # MKCF8528, 0.7 mol % ketone functionalization, branching = 39 Me/1000C). Precipitation from MeOH, centrifugation and drying overnight yielded **11** (17.6 mg, 1.9 mol % N_3-Functionalization, 36 Me/1000C) as a pale brown solid. The aliphatic signals between 2.20–0.39 ppm were integrated to a total of 400. The proton adjacent to the azide moiety that appear at 3.20 ppm was used to determine the mol % of the secondary C(sp^3)–H azidation (0.5 mol %) per repeat unit as demonstrated in section **2**. However, the total level of functionalization determined by elemental analysis (2.3 mol %) and the ^{1}H NMR analysis of the 1,3-cycloaddition product with dimethyl acetylenedicarboxylate (2.4 mol %) indicate that the C(sp^3)–H azidation mainly took place on the tertiary C–H of the polymer branches. The ration 3° to 2° azidation equals 3.8:1.0. The ketone functionalization occurred up to 0.8 mol %. The selectivity for azidation versus oxygenation equals to 2.9:1.0. The branching was determined by ^{1}H NMR analysis as 36 Me/1000C.[9] For elemental analysis the sample was dissolved in tetrachloroethane at 80 °C and reprecipitated in MeOH and dried *in vacuo* for 48 h at 60 °C.

^{1}H NMR (600 MHz, $C_2D_2Cl_4$, 75°C) δ 3.38–3.16 (br, 0.54H, CH), 2.61–2.28 (t, J = 7.0 Hz, 5.98H, CH_2), 2.20–1.04 (br, 400H), 1.03–0.39 (br, 23H).

^{13}C NMR (126 MHz, $C_2D_2Cl_4$, 75°C) δ 67.0 (C_q), 63.5 (CH), 44.2–41.8 (2 x CH_2), 35.2–21.4 (4 x CH_2), 14.6–10.0 (CH_3). One C_q is missing due to low signal to noise ratio.

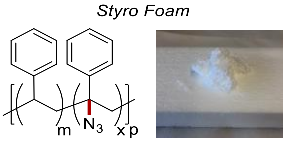
IR (ATR): $\tilde{\nu}$ = 2915, 2850, 2095 (azide N_3 stretching), 1718 (carbonyl CO stretching), 1465, 1370, 1253, 1106, 1033, 812, 723 cm^{-1}.

DSC (°C, 10 °C/min): Parent: T_m = 104.7; Functionalized: T_m = 104.2.

TGA (°C, 20 °C/min): Parent: T_{deg} = 446.5; Functionalized: T_{deg} = 445.1.

Elemental Analysis: calcd. for $C_{2x}H_{4-x}N_{3x}$ with x = 0.023 C 82.50 H 13.70 N 3.25, found C 79.40 H 12.65 N 3.23.

Polystyrene-Azide – From Stryo Foam **12**



12

The general procedure **GP1** was followed using styro foam (104 mg, 1.0 mmol, M_w = 248 kDa, $Đ$ = 2.60). Precipitation from MeOH yielded **12** (59.4 mg, M_w = 195 kDa, $Đ$ = 2.63, 1.9 mol % N_3-Functionalization) as a white solid. Upon purification the percent of azide moieties were determined by correlating the relative IR intensity of the N_3- and CH-band with level of functionalization of the 1,3-cycloaddition product from section **2.** For this purpose, the area in the IR spectrum from $\tilde{\nu}$ = 3047 cm^{-1} – 2995 cm^{-1} (benzylic C–H band) and from $\tilde{\nu}$ = 2153 cm^{-1} – 2040 cm^{-1} (azide band) were integrated. The following ^{13}C NMR data was collected using at least 50 mg of **12** from the 1st run.

1st run: 59.4 mg, M_w = 186 kDa, $Đ$ = 2.67, 1.9 mol % N_3-Functionalization

2nd run: 61.9 mg, M_w = 194 kDa, $Đ$ = 2.60, 1.9 mol % N_3-Functionalization

3rd run: 68.9 mg, M_w = 195 kDa, $Đ$ = 2.63, 1.9 mol % N_3-Functionalization

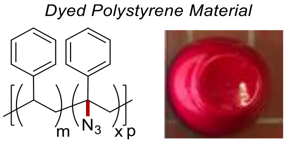
^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.37–6.94 (br, 300H), 6.87–6.30 (br, 200H), 2.45−1.70 (br, 100H), 1.69−1.22 (br, 200H).

^{13}C NMR (126 MHz, CD_2Cl_2) δ 146.2−145.4 (C_q), 140.9 (C_q), 128.5−127.2 (4 x CH), 126.6−125.8 (2 x CH), 70.6 (C_q), 48.6−41.4 (2 x CH_2), 41.3−39.1 (CH).

IR (ATR): $\tilde{\nu}$ = 3065, 3026, 2922, 2851, 2106 (azide N_3 stretching), 1945, 1875, 1806, 1744, 1599, 1493, 1450, 1026, 753, 698, 542 cm^{-1}.

GPC (THF): Parent: M_w = 248 kDa, $Đ$ = 2.60; Functionalized: M_w = 195 kDa, $Đ$ = 2.63.

Polystyrene-Azide – From Dyed Polystyrene Material **13**



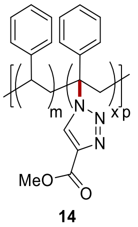
13

The general procedure **GP1** was followed using post-consumer polystyrene (104 mg, 1.0 mmol, 1.0 equiv, M_w = 247 kDa, $Đ$ = 2.64). Precipitation from MeOH yielded **13** (66.9 mg, M_w = 212 kDa, $Đ$ = 2.66, 1.6 mol % N_3-Functionalization) as a white solid. Upon purification the percent of azide moieties were

determined by correlating the relative IR intensity of the N_3- and CH-band with level of functionalization of the 1,3-cycloaddition product from section **2**. For this purpose, the area in the IR spectrum from $\tilde{\nu}$ = 3047 cm^{-1} – 2995 cm^{-1} (benzylic C–H band) and from $\tilde{\nu}$ = 2153 cm^{-1} – 2040 cm^{-1} (azide band) were integrated. The following ^{13}C NMR data was collected using at least 50 mg of **13** from the 1st run.
1st run: 66.9 mg, M_w = 215 kDa, $Đ$ = 2.67, 1.6 mol % N_3-Functionalization
2nd run: 63.1 mg, M_w = 212 kDa, $Đ$ = 2.66, 1.8 mol % N_3-Functionalization
3rd run: 74.2 mg, M_w = 213 kDa, $Đ$ = 2.79, 1.5 mol % N_3-Functionalization

^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.37–6.94 (br, 300H), 6.87–6.30 (br, 200H), 2.45–1.70 (br, 100H), 1.69–1.22 (br, 200H).
^{13}C NMR (126 MHz, CD_2Cl_2) δ 146.2–145.4 (C_q), 141.0 (C_q), 128.5–127.2 (4 x CH), 126.6–125.8 (2 x CH), 70.7 (C_q), 48.6–41.4 (2 x CH_2), 41.3–39.1 (CH).
IR (ATR): $\tilde{\nu}$ = 3065, 3026, 2915, 2851, 2106 (azide N_3 stretching), 1945, 1875, 1806, 1744, 1590, 1487, 1446, 1026, 753, 698, 542 cm^{-1}.
GPC (THF): Parent: M_w = 247 kDa, $Đ$ = 2.64; Functionalized: M_w = 215 kDa, $Đ$ = 2.67.

Methyl 1-(polystyrene)- 1*H* -1,2,3-triazole-4-carboxylate **14**

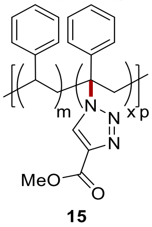


14

The general procedure **GP2** was followed using **3** (21 mg, 0.20 mmol, 1.0 equiv). Precipitation from MeOH yielded the product **14** (8.6 mg) as an off-white solid. The level of functionalization of **14** was determined as 1.8 mol % by ^{1}H NMR as described in section **2**.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.37–6.78 (br, 300H), 6.77–6.07 (br, 200H), 3.92–3.66 (br, 5.53H, CH_3), 2.33–1.66 (br, 100H), 1.65–1.25 (br, 200H).
^{13}C NMR (126 MHz, CD_2Cl_2) δ 161.4 (C_q), 146.9–144.2 (2 x $C_{q,}$), 142.1 (C_q), 129.0–126.7 (4 x CH), 126.6–125.6 (2 x CH), 52.5–50.7 (CH_3), 47.6–41.6 (2 x CH_2), 41.5–37.9 (CH).
IR (ATR): $\tilde{\nu}$ = 3046, 3009, 2915, 2850, 1930, 1857, 1794 (carbonyl CO stretching), 1733 (carbonyl CO stretching), 1712, 1492, 1449, 1027, 755, 698, 542 cm^{-1}.
GPC (THF): Parent: M_w = 199 kDa, $Đ$ = 2.72; Functionalized: M_w = 203 kDa, $Đ$ = 2.58.

Methyl 1-(polystyrene)- 1*H*-1,2,3-triazole-4-carboxylate **15**



15

The general procedure **GP2** was followed using **4** (6.7 mol % N_3-Functionalization by IR-^{1}H NMR correlation, 42 mg, 0.40 mmol, 1.0 equiv). Precipitation from MeOH yielded the product **15** (30 mg) as an off-white solid. The level of functionalization of **15** was determined as 6.7 mol % by ^{1}H NMR as described in section **2**. The

TG-analysis was performed at 15 °C/min heating rate to check if partial weight loss takes place before the total material degradation at T_{deg}.

^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.73–6.84 (br, 300H), 6.83–5.68 (br, 200H), 4.32–3.25 (br, 20.02H, CH_3), 2.33–1.66 (br, 100H), 1.65–1.25 (br, 200H).

^{13}C NMR (126 MHz, CD_2Cl_2) δ 161.3 (C_q), 147.2–144.2 (2 x $C_{q,}$), 141.7 (C_q), 139.0 (C_q), 130.0–126.8 (4 x CH), 126.7–124.5 (2 x CH), 71.2 (C_q), 52.2–50.8 (CH_3), 48.3–41.6 (2 x CH_2), 41.5–36.5 (CH).

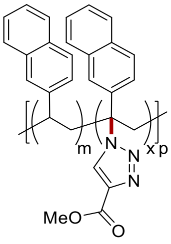
IR (ATR): $\tilde{\nu}$ = 3046, 3009, 2915, 2850, 1930, 1857, 1794 (carbonyl CO stretching), 1733 (carbonyl CO stretching), 1712, 1492, 1449, 1027, 755, 698, 542 cm^{-1}.

DSC (°C, 10 °C/min): Parent: T_g = 104.1; Functionalized: T_g = 120.3.

TGA (°C, 15 °C/min): Parent: T_{deg} = 339.7; Functionalized: T_{deg} = 346.5.

GPC (THF): Parent: M_w = 16.5 kDa, $Đ$ = 1.14; Functionalized: M_w = 16.8 kDa, $Đ$ = 1.12.

Methyl 1-(poly(2-vinylnaphatlene))- 1*H*-1,2,3-triazole-4-carboxylate **16**



16

The general procedure **GP2** was followed using **6** (33.3 mg, 0.20 mmol, 1.0 equiv). Precipitation from MeOH yielded the product **16** (19.4 mg) as off-white solid.

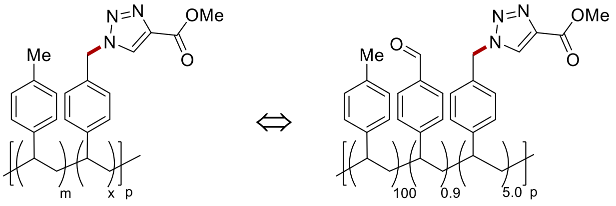
^{1}H NMR (600 MHz, CD_2Cl_2) δ 8.28–5.69 (br, 700H), 3.94–3.14 (br, 7.79H, CH_3), 2.84–1.75 (br, 100H), 1.70–0.42 (br, 200H).

^{13}C NMR (126 MHz, CD_2Cl_2) δ 144.3–141.6 (2 x C_q), 134.1–132.8 (2 x C_q), 132.7–131.8 (2 x C_q), 128.5–124.1 (14 x CH), 52.5–50.1 (CH_3), 46.8–41.3 (2 x CH_2), 41.2–39.7 (CH). Two C_q are missing due to low signal to noise ratio or signal overlap.

IR (ATR): $\tilde{\nu}$ = 3046, 3009, 2915, 2850, 1949, 1876, 1805, 1741 (carbonyl CO stretching), 1600, 1492, 1449, 1027, 755, 698, 542 cm^{-1}.

GPC (THF): Parent: M_w = 41 kDa, $Đ$ = 1.09; Functionalized: M_w = 44 kDa, $Đ$ = 1.25.

Methyl 1-(poly(4-vinylbenzyl)-1*H*-1,2,3-triazole-4-carboxylate **17**



17

The general procedure **GP2** using **7** (25.5 mg, 0.20 mmol, 1.0 equiv). Precipitation from MeOH yielded the product **17** (16.8 mg) as off-white solid.

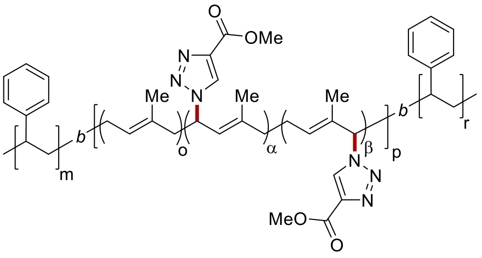
^{1}H NMR (600 MHz, $CDCl_3$) δ 10.0–9.75 (br, 0.95, CHO), 8.08–7.68 (br, 4.44H, CH), 7.20–6.67 (br, 200H), 6.66–5.95 (br, 200H), 5.73–5.09 (br, 8.27H, CH_2), 4.33–3.62 (br, 14.86H, CH_3), 2.59–2.07 (br, 300H), 2.06–1.61 (br, 100H), 1.60–0.93 (br, 200H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 192.2 (CHO), 161.3–161.1 (C_q), 143.7–141.7 (3 x C_q), 140.4–140.2 (C_q), 135.4–134.1 (3 x C_q), 129.2–128.2 (3 x CH), 128.1–127.0 (4 x CH), 54.5–54.2 (CH_2), 52.4–52.2 (CH_3), 48.3–41.0 (3 x CH_2), 40.9–39.3 (3 x CH), 21.8–20.6 (CH_3).

IR (ATR): $\tilde{\nu}$ = 3096, 3053, 3023, 2924, 2849, 1906, 1800, 1740 (carbonyl CO stretching), 1721 (carbonyl CO stretching), 1712, 1610, 1517, 1450, 1371, 1227, 1181, 1115, 1028, 817, 729, 548 cm^{-1}.

GPC (THF): Parent: M_w = 180 kDa, Đ = 4.69; Functionalized: M_w = 130 kDa, Đ = 3.28.

Methyl 1-(polystyrene-*b*-isoprene-*b*-polystyrene)-1*H*-1,2,3-triazole-4-carboxylate **18**



18

The general procedure **GP2** was followed using **10** (15.3 mg, 0.20 mmol, 1.0 equiv). Precipitation from MeOH yielded the product **18** (7.4 mg) as off-white solid.

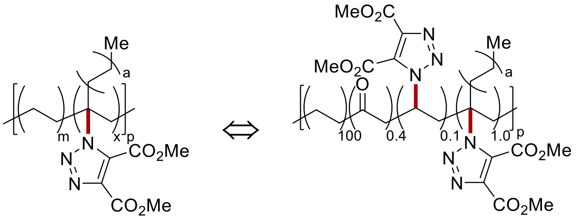
^{1}H NMR (600 MHz, CD_2Cl_2) δ 8.30–7.96 (br, 29.33H, CH), 7.38–6.88 (br, 300H), 6.87–6.36 (br, 200H), 5.26–4.90 (br, 169H, CH), 4.86–4.70 (d, *J* = 13.3 Hz, 24H), 4.69–4.58 (d, *J* = 15.0 Hz, 13H), 3.80–3.57 (br, 200.2H, CH_3), 2.90–2.30 (br, 172H), 2.29–1.74 (br, 1117H), 1.73–0.42 (br, 1814H).

^{13}C NMR (126 MHz, CD_2Cl_2) δ 162.7–161.0 (C_q), 148.2–144.5 (C_q), 141.0–138.5 (C_q), 129.0–126.9 (CH), 126.5–122.4 (CH), 113.2–109.5 (CH_2), 65.0–60.3 (CH_3), 53.7–49.9 (CH), 49.9–47.8 (CH_3), 47.5–42.3 (CH_2), 42.2–41.4 (CH), 41.3–39.2 (CH and CH_2), 39.1–37.8 (CH_2), 38.0–36.0 (CH_2), 33.7–32.7 (CH_2), 32.6–31.5 (CH_2), 31.4–30.1 (CH_2), 30.0–28.8 (CH_2), 27.8–25.7 (CH_2), 24.3–23.1 (CH_3 and CH_2), 19.7–17.9 (CH_3), 17.3–15.4 (CH_3). Four C_q are missing due to signal overlap.

IR (ATR): $\tilde{\nu}$ = 2967, 2918, 2850, 1722 (carbonyl CO stretching), 1448, 1369, 1199, 953, 697 cm^{-1}

GPC (THF): Parent: M_w = 168 kDa, Đ = 2.59; Functionalized: M_w = 95 kDa, Đ = 7.90.

Methyl 1-(polyethlyene)-1*H*-1,2,3-triazole-4,5-dicarboxylate **19**



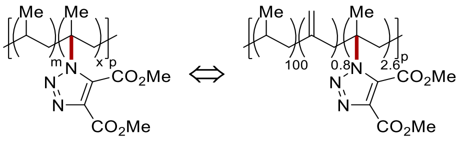
9click

The general procedure **GP3** was followed using **9** (11.2 mg, 0.40 mmol, 1.0 equiv). Precipitation from MeOH yielded the product **19** (7.8 mg) as a light yellow solid.

^{1}H NMR (600 MHz, $C_2D_2Cl_4$, 75 °C) δ 4.70 (br, 0.07, CH), 4.21–3.20 (br, 6.24H, CH_3), 2.45–2.35 (t, *J* = 7.3 Hz, 0.78H, CH_2), 2.26–1.05 (br, 400 H), 1.04–0.69 (br, 15H).

^{13}C NMR (126 MHz, $C_2D_2Cl_4$, 75°C) δ 54.0−50.6 (CH_3), 43.8–41.9 (2 x CH_2), 38.3–21.4 (4 x CH_2), 15.1–12.9 (CH_3). Five C_q are missing due to low signal to noise ratio.
IR (ATR): $\tilde{\nu}$ = 2916, 2848, 1736 (carbonyl CO stretching), 1646 (carbonyl CO stretching), 1462, 1260, 1091, 802, 719 cm^{-1}.

Dimethyl 1-(polypropylene)-1*H*-1,2,3-triazole-4,5-dicarboxylate **20**

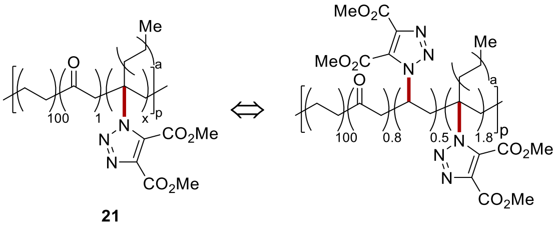


20

The general procedure **GP3** was followed using **10** (10.0 mg, 0.21 mmol, 1.0 equiv). Precipitation from MeOH yielded the product **20** (3.4 mg) as a brown solid.

^{1}H NMR (600 MHz, $C_2D_2Cl_4$, 75 °C) δ 4.75 (s, 1.58H, CH_2), 4.26–3.52 (br, 15.82H, CH_3), 2.20–1.46 (br, 100H), 1.35–1.13 (br, 100H), 1.05–0.19 (br, 400H).
^{13}C NMR (126 MHz, $C_2D_2Cl_4$, 75°C) δ 54.2−52.1 (CH_3), 48.4−43.9 (2x CH_2), 29.9−26.9 (CH), 23.2−19.6 (2 x CH_3). Six C_q, and one CH_2 are missing due to low signal to noise ratio.
IR (ATR): $\tilde{\nu}$ = 2951, 2916, 2874 2834, 1723 (carbonyl CO stretching), 1452, 1371, 798 cm^{-1}.

Dimethyl 1-(polyethylene)-1*H*-1,2,3-triazole-4,5-dicarboxylate **21**

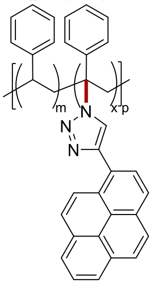


21

The general procedure **GP3** was followed using **11** (11.2 mg, 0.40 mmol, 1.0 equiv). Precipitation from MeOH yielded the product **21** (8.7 mg) as a light yellow solid.

^{1}H NMR (600 MHz, $C_2D_2Cl_4$, 75 °C) δ 4.72 (tt, *J* = 9.4, 5.0 Hz, 0.53H, CH), 4.23–3.35 (br, 11.53H, CH_3), 2.53–2.29 (t, *J* = 7.0 Hz, 3.05H, CH_2), 2.20–1.00 (br, 400H), 1.00–0.56 (br, 22H).
^{13}C NMR (126 MHz, $C_2D_2Cl_4$, 75°C) δ 160.9 (C_q), 139.0 (C_q), 63.5 (CH), 54.7−51.5 (CH_3), 45.2−41.7 (CH_2), 40.1−22.0 (CH_2), 15.4−0.3 (CH_3). Two C_q are missing due to low signal to noise ratio.
IR (ATR): $\tilde{\nu}$ = 2915, 2846, 1736 (carbonyl CO stretching), 1557, 1463, 1223, 719 cm^{-1}.

1-(polystyrene)-4-pyren-1-yl-1*H*-1,2,3-triazole **22**



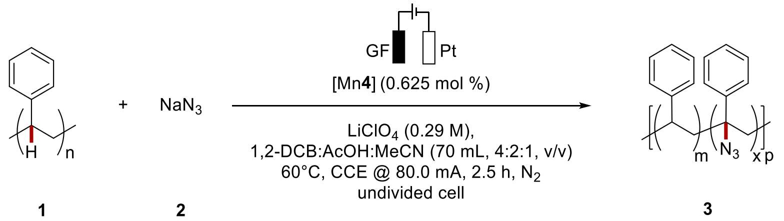
22

The general procedure **GP2** was followed using **12** from scale-up (104 mg, 1.0 mmol, M_w = 204 kDa, $Đ$ = 2.66, 0.8 mol % N_3-functionalization) and 1-ethynylpyrene (114 mg, 0.5 mmol, 0.5 equiv.). Precipitation from MeOH (15 mL), redissolved in DCM (5 mL) and precipitation from acetone (15 mL) two times and a final precipitation from MeOH (15 mL) yielded **22** (59.4 mg, M_w = 255 kDa, $Đ$ = 1.72, 0.5 mol % triazole-Functionalization) as a yellow solid. The conversion was determined as quantitative as the azide band in the IR spectrum was completely vanished. Upon purification the percent of triazole moieties were determined by ^{1}H NMR analysis. For this purpose, the signals between 2.20–0.39 ppm were integrated to a total of 500. The protons of the pyrenyl moiety that appear between 8.97–7.44 ppm were used to determine the mol % per repeat unit. As this signal refers to the 9 protons, the level of functionalization of **22** equals to 0.5 mol %.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97–7.44 (br, 5.17H), 7.26–6.81 (br, 300H), 6.80−5.82 (br, 200H), 3.08−1.69 (br, 100H), 1.68−0.37 (br, 200H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 147.1−143.0 (C_q), 131.7−130.5 (C_q), 129.7−123.9 (15 x CH), 123.8−122.0 (5 x C_q), 70.1 (C_q), 47.6−41.2 (2 x CH_2), 41.1−39.9 (CH).
IR (ATR): $\tilde{\nu}$ = 3065, 3026, 2922, 2851, 1945, 1875, 1806, 1744, 1599, 1493, 1450, 1026, 753, 698, 542 cm^{-1}.
DSC (°C, 10 °C/min): Parent: T_g = 107.1; Functionalized: T_g = 107.7.
TGA (°C, 20 °C/min): Parent: T_{deg} = 391.2; Functionalized: T_{deg} = 396.3.
GPC (THF): Parent: M_w = 204 kDa, $Đ$ = 2.55; Functionalized: M_w = 255 kDa, $Đ$ = 1.72.

7. Scale Up Electrolysis

7.1. 20 mmol Scale-up



1
M_w = 238 kDa
$Đ$ = 2.77
2.08 g
20.0 mmol
(Monomer Unit)

2
4.0 equiv

3
Recovered material = 1.56 g
M_w = 206 kDa (87%)
$Đ$ = 2.55
Level of Functionalization = 1.1 mol %
Mn-Contamination = 8.56 ppm

The electrocatalysis was carried out in an undivided cell with graphite felt (GF) anodic (40 mm × 50 mm × 6 mm) and a platinum cathode (25 mm × 50 mm × 0.25 mm). A stock solution of **1** (2.08 g, 20 mmol, 1.0 equiv, M_w = 238 kDa, $Đ$ = 2.77) in 1,2-DCB (40 mL) was degassed by three frezz-pump-thaw cycles. MeCN and AcOH were degassed by bubbling N_2 *via* a syringe for 1.0 h. **2** (5.20 g, 80 mmol, 4.0 equiv), $LiClO_4$ (2.12 g, 20 mmol, 1.0 equiv) and [Mn4] (92 mg, 0.125 mmol, 0.625 mol %) were placed in a 150 mL reactor and were evacuated and backfilled with N_2 three times. Then, the stock solution of **1** in 1,2-DCB (0.5 M, 40 mL) was transferred under N_2. The reactor was allowed to equilibrate at 60 °C for 30 min. Afterwards, degassed MeCN (10 mL) and AcOH (20 mL) were added. After 20 min equilibration, the electrolysis was initiated with 80 mA for 2.5 h (0.36 F/mol). After the electrolysis, the reaction mixture was poured in MeOH (400 mL), redissolved in DCM (200 mL), filtered over celite and precipitated in MeOH (400 mL) to obtain a white azide-modified polystyrene **3** (1.56 g, M_w = 206 kDa, $Đ$ = 2.55, 1.1 mol %). Upon purification the percent of azide moieties were determined by correlating the relative IR intensity of the N_3- and CH-band with level of functionalization of the 1,3-cycloaddition product from section **2**. For this purpose, the area in the IR spectrum from $\tilde{\nu}$ = 3047 cm^{-1} – 2995 cm^{-1} (benzylic C–H band) and from $\tilde{\nu}$ = 2153 cm^{-1} – 2040 cm^{-1} (azide band) were integrated.

For ICP-MS analysis **3** (200 mg) were digested in HNO_3 (trace metal grade, 6.0 mL) were digested at 120 °C for 48 h in a new pressure tube. Then, the mixture was diluted to a volume of 30 mL with water (LC-MS grade, 24 mL) and transferred into a new falcon tube. After centrifugation, the supernatant was decanted and analyzed on a Thermo Scientific™ iCAP™ RQ.

IR (ATR): $\tilde{\nu}$ = 3065, 3026, 2915, 2851, 2106 (azide N_3 stretching), 1945, 1875, 1806, 1744, 1590, 1487, 1446, 1026, 753, 698, 542 cm^{-1}.

GPC (THF): Parent: M_w = 238 kDa, $Đ$ = 2.77; Functionalized: M_w = 206 kDa, $Đ$ = 2.55.

ICP-MS: 8.56 ppm Mn Contamination.

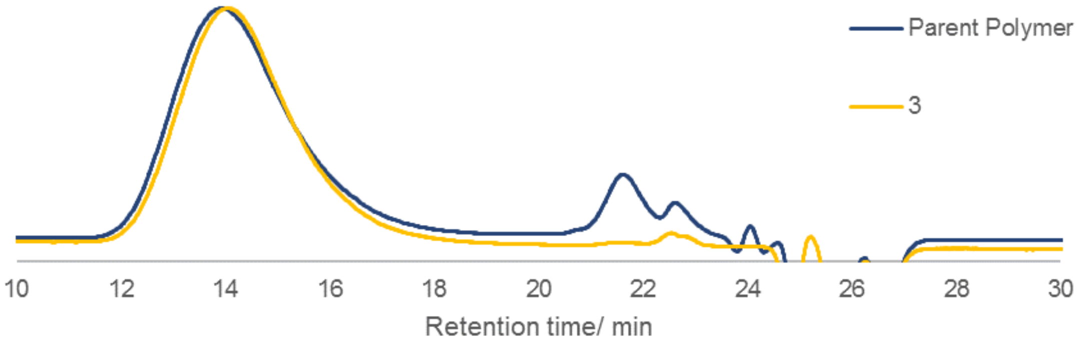


Figure S5. Normalized chromatogram of the parent (blue) and modified polymer **3** (yellow).

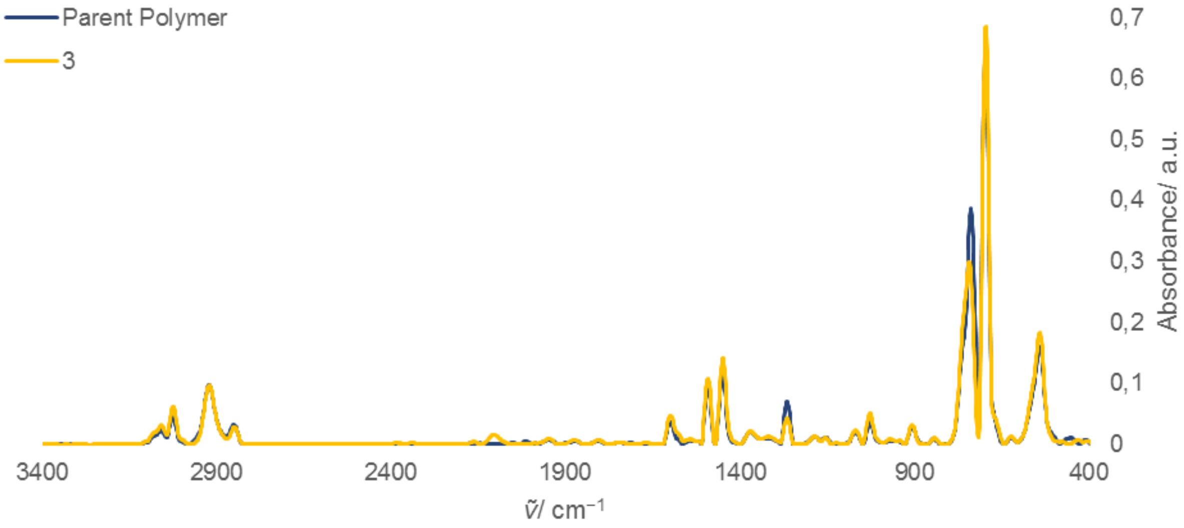


Figure S6. IR spectrum of the parent (blue) and modified polymer **3** (yellow).

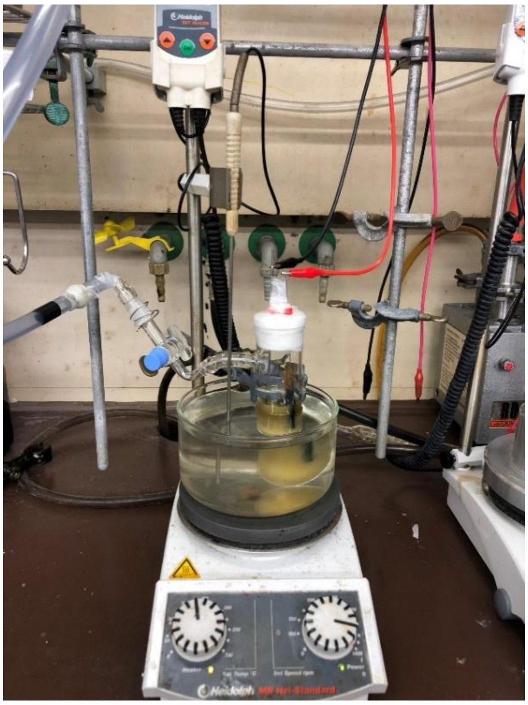
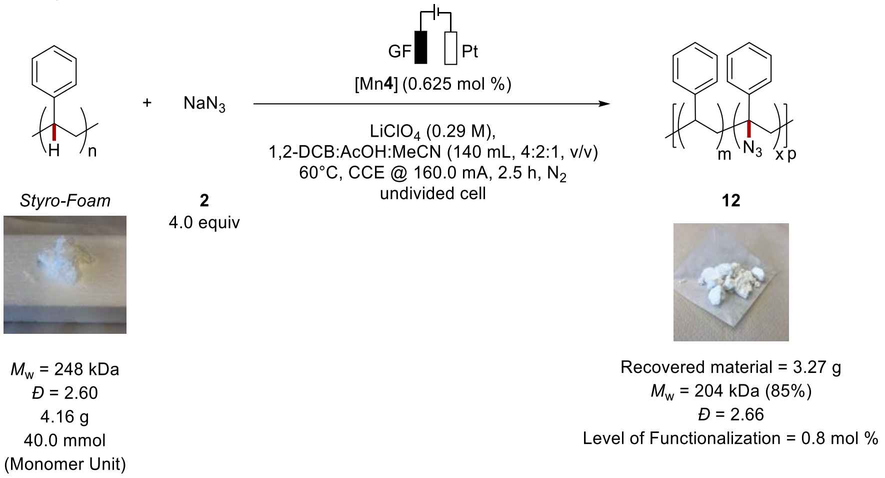


Figure S7. Picture of the scale-up set up.

7.2. 40 mmol Scale-up



The electrocatalysis was carried out in an undivided cell with graphite felt (GF) anodes (40 mm × 50 mm × 6 mm) and a platinum cathode (25 mm × 50 mm × 0.25 mm). A stock solution of styro foam (4.16 g, 40 mmol, 1.0 equiv, M_w = 248 kDa, $Đ$ = 2.60) in 1,2-DCB (80 mL) was degassed by three frezz-pump-thaw cycles. MeCN and AcOH were degassed by bubbling N$_2$ *via* a syringe for 1.0 h. **2** (10.40 g, 160 mmol, 4.0 equiv), LiClO$_4$ (4.24 g, 40 mmol, 1.0 equiv) and [Mn4] (184 mg, 0.25 mmol, 0.625 mol %) were placed in a 250 mL reactor and were evacuated and backfilled with N$_2$ three times. Then, the stock solution of styro foam in 1,2-DCB (0.5 M, 80 mL) was transferred under N$_2$. The reactor was allowed to equilibrate at 60 °C for 30 min. Afterwards, degassed MeCN (20 mL) and AcOH (40 mL) were added. After 20 min equilibration, the electrolysis was initiated with 160 mA for 2.5 h (0.36 F/mol). After the electrolysis, the reaction mixture was poured in MeOH (400 mL), redissolved in DCM (200 mL), filtered over celite and precipitated in MeOH (400 mL) to obtain a white azide-modified polystyrene **12** (3.27 g, M_w = 204 kDa, $Đ$ = 2.66, 0.8 mol %). Upon purification the percent of azide moieties were determined by correlating the relative IR intensity of the N$_3$- and CH-band with level of functionalization of the 1,3-cycloaddition product from section **2**. For this purpose, the area in the IR spectrum from $\tilde{\nu}$ = 3047 cm^{-1} – 2995 cm^{-1} (benzylic C–H band) and from $\tilde{\nu}$ = 2153 cm^{-1} – 2040 cm^{-1} (azide band) were integrated.

IR (ATR): $\tilde{\nu}$ = 3065, 3026, 2915, 2851, 2106 (azide N$_3$ stretching), 1945, 1875, 1806, 1744, 1590, 1487, 1446, 1026, 753, 698, 542 cm^{-1}.
DSC (°C, 10 °C/min): Parent: T_g = 106.0; Functionalized: T_g = 107.1.
TGA (°C, 20 °C/min): Parent: T_{deg} = 400.4; Functionalized: T_{deg} = 391.2.
GPC (THF): Parent: M_w = 248 kDa, $Đ$ = 2.60; Functionalized: M_w = 204 kDa, $Đ$ = 2.66.

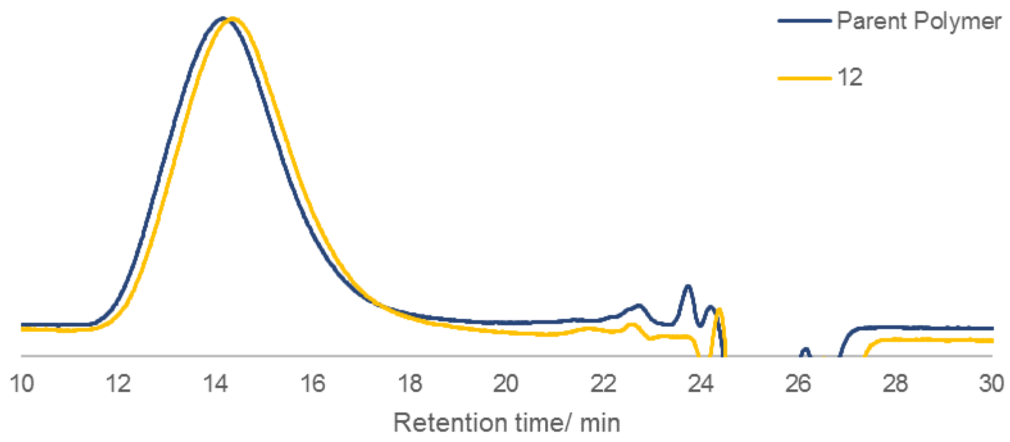


Figure S8. Normalized chromatogram of the parent (blue) and modified polymer **12** (yellow).

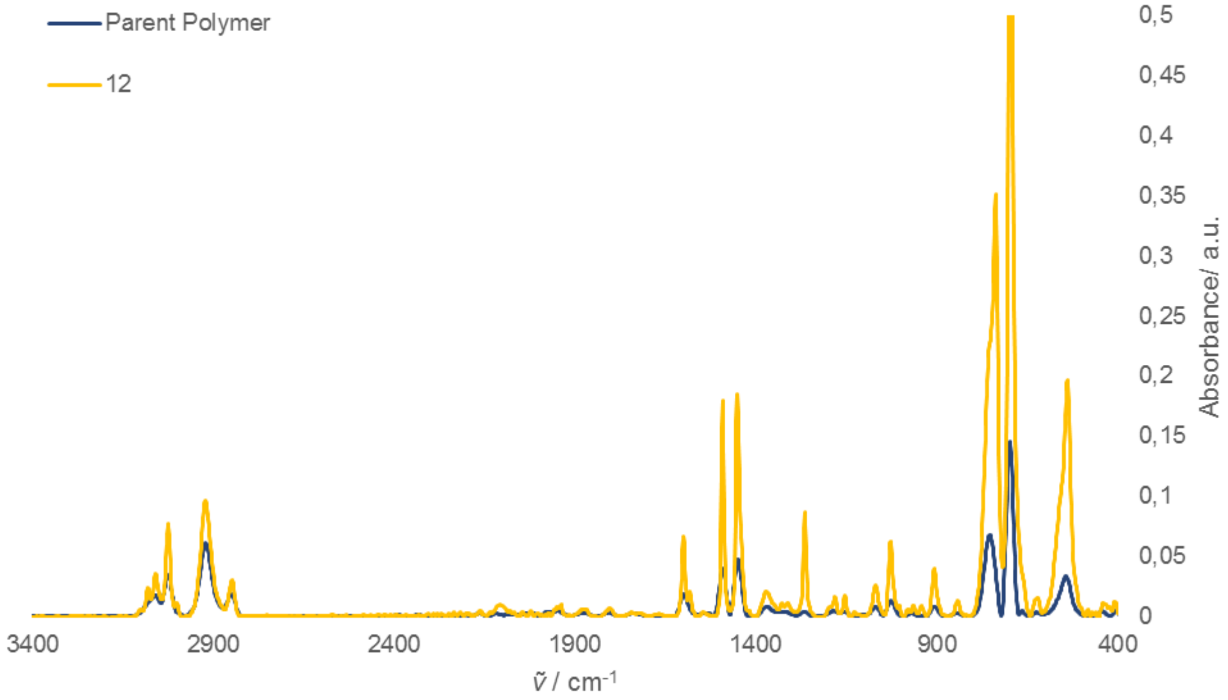


Figure S9. IR spectrum of the parent (blue) and modified polymer **12** (yellow).

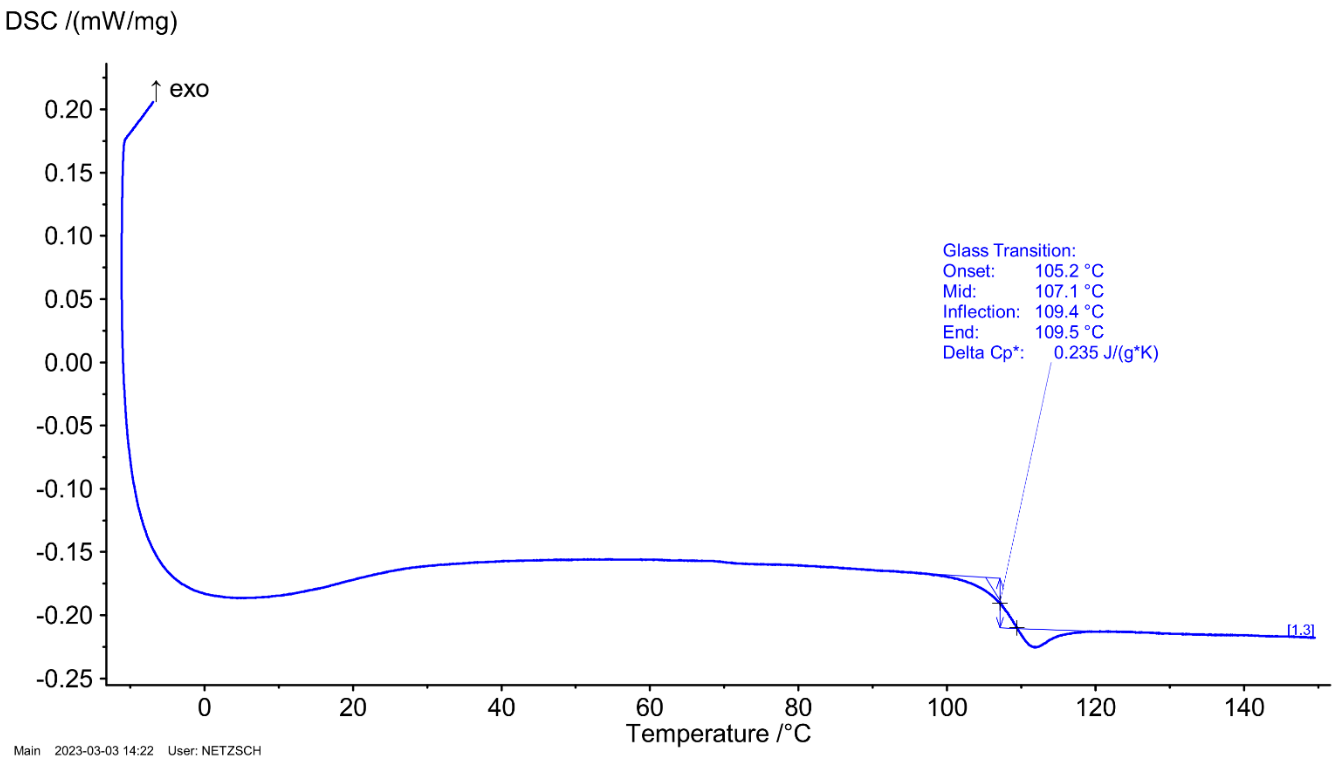


Figure S10. DSC of **12**.

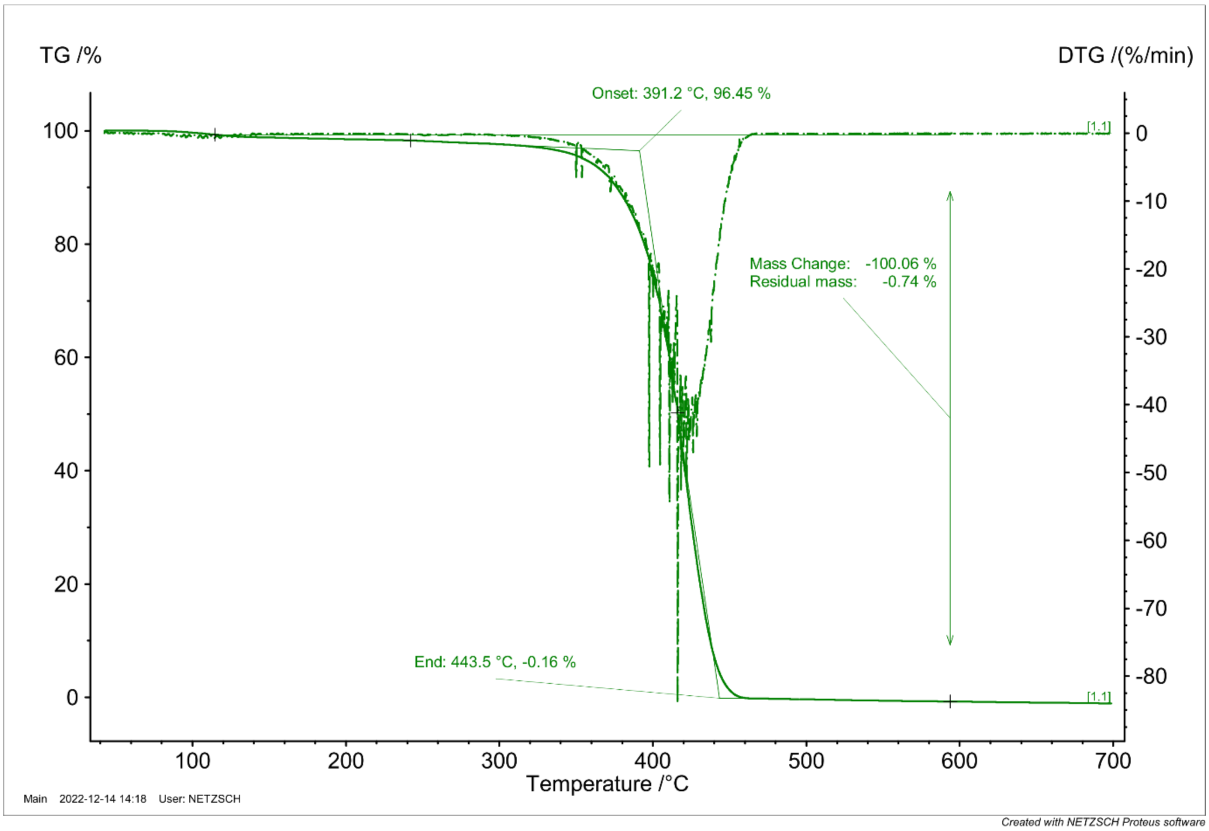
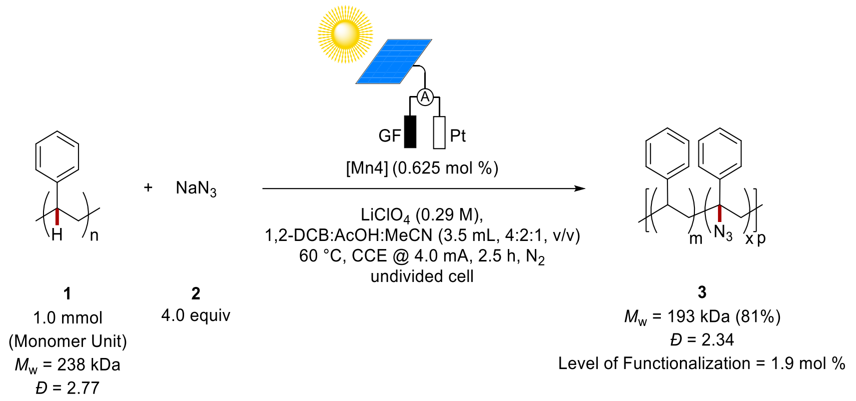


Figure S11. TGA of **12**.

Figure S12. Picture of the scale-up set up.

8. Solar Panel supplied Electrolysis



For the solar panel powered electrocatalysis, a commercially available photovoltaic cell (Conrad Electronic SE, TPS-103 6 W, 17.5 V max. voltage, 428 mA max. current, 467 mm x 161 mm x 19 mm) was used. The output was regulated with a customized and normalized constant current regulator and double checked with an ammeter.

The electrocatalysis was conducted in an undivided cell, with a GF anode (10 mm x 15 mm x 3 mm) and a platinum electrode (10 mm x 15 mm x 0.25 mm). A 10 mL cell was charged with **1** (1.0 mmol, 1.0 equiv, M_w = 238 kDa, $Đ$ = 2.77, Thermo Scientific), **2** (4.0 mmol, 4.0 equiv) and $LiClO_4$ (1.0 mmol, 1.0 equiv). Then, 1 mL of a [Mn4] stock solution, prepared from 23 mg [Mn4] in 1,2-DCB (3.0 mL), 1,2-DCB (1.0 mL) were added under N_2. After stirring at 60 °C for 1.0 h to dissolve the polymer beads, MeCN (0.5 mL) and AcOH (1.0 mL) were added, and the electrodes equipped. The electrolysis was initiated at 4.0 mA and 60 °C for 2.5 h on the 16.09.22 between 11:35 and 14:05. After the electrolysis, the reaction mixture was filtered over celite, poured in MeOH (50 mL), washed with MeOH (20 mL), water (2 x 5 mL), MeOH (20 mL) to afford **3** (75.7 mg, M_w = 193 kDa, $Đ$ = 2.34, 1.9 mol %). Upon purification the percent of azide moieties were determined by correlating the relative IR intensity of the N_3- and CH-band with level of functionalization of the 1,3-cycloaddition product from section **2**. For this purpose, the area in the IR spectrum from $\tilde{\nu}$ = 3047 cm^{-1} – 2995 cm^{-1} (benzylic C–H band) and from $\tilde{\nu}$ = 2153 cm^{-1} – 2040 cm^{-1} (azide band) were integrated.

IR (ATR): $\tilde{\nu}$ = 3065, 3026, 2915, 2851, 2106 (azide N_3 stretching), 1945, 1875, 1806, 1744, 1590, 1487, 1446, 1026, 753, 698, 542 cm^{-1}.

GPC (THF): Parent: M_w = 238 kDa, $Đ$ = 2.77; Functionalized: M_w = 193 kDa, $Đ$ = 2.34.

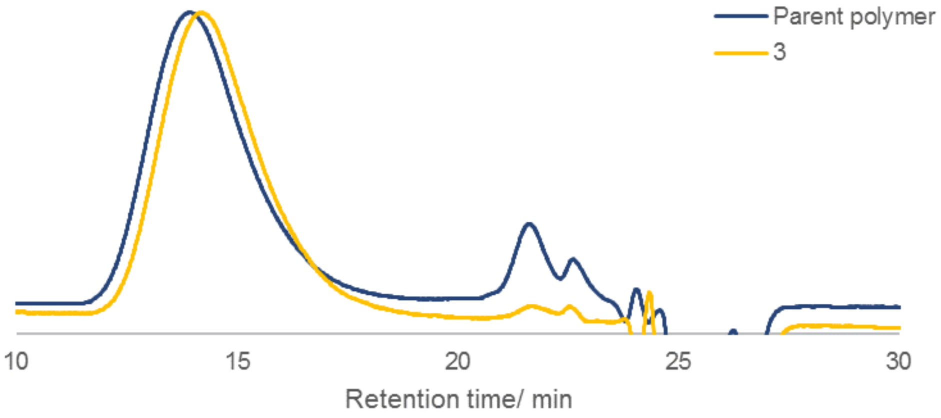


Figure S13. Normalized chromatogram of the parent (blue) and modified polymer **3** (yellow).

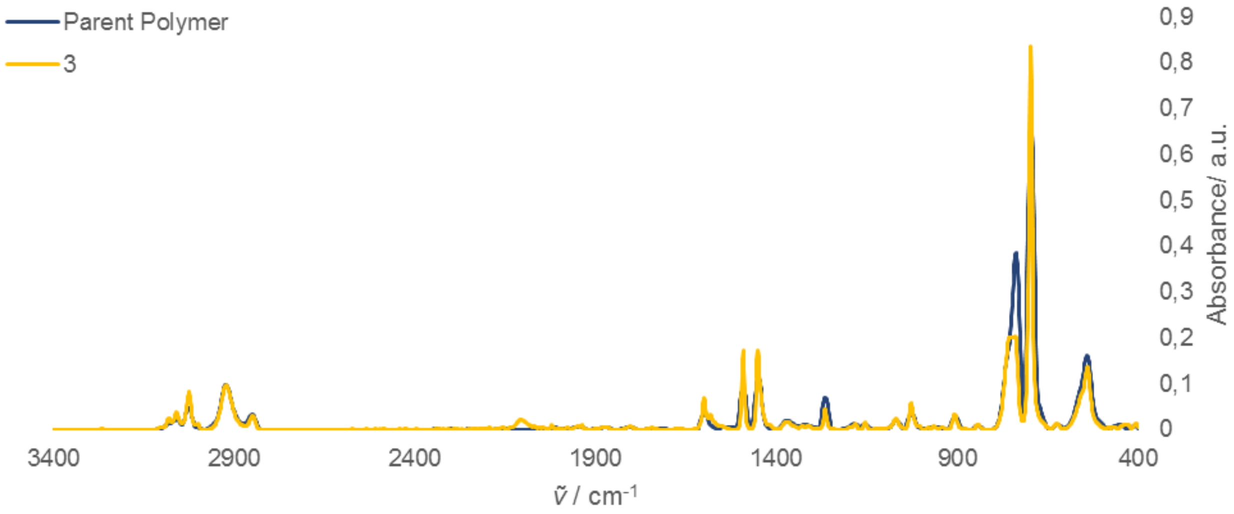


Figure S14. IR spectrum of the parent (blue) and modified polymer **3** (yellow).

9. Fluorescence study of 22

Sample preparation:

10 mg of **22** were dissolved in DCM (1.0 mL). Then, 100 µL of this stock solution were added to 100 mg of styro foam in DCM (10 mL) to give a solution of 1.0 wt% of **22**.

To obtain a sample of 3 wt% of **22**, further 200 µL of the stock solution of **22** were added to the above mentioned solution.

Of each solution one drop was casted on a glass plate.

10. Thermal stability and mechanical properties of azide products

10.1. Analysis of thermal stability of 4

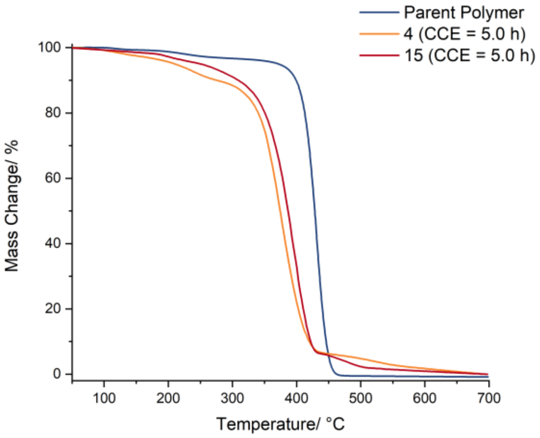


Figure S15. TGA of parent polymer of **4** (dark blue), **4** after 5.0 h of CCE (orange) and **15** (red). In case of **4** and **15**, the trace was normalized. The residual mass was 15% and 9% were for **4** and **15**, respectively.

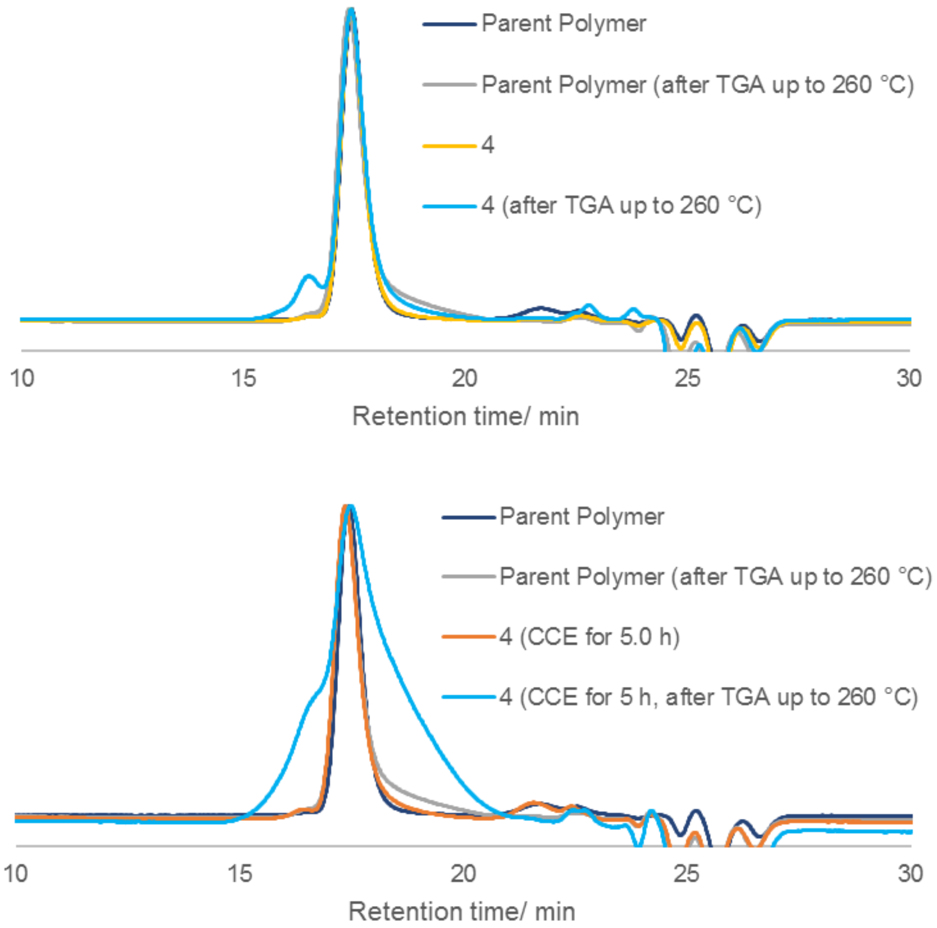


Figure S16. GPC traces of **4** after 2.5 h (top) and 5.0 h (bottom) of CCE.

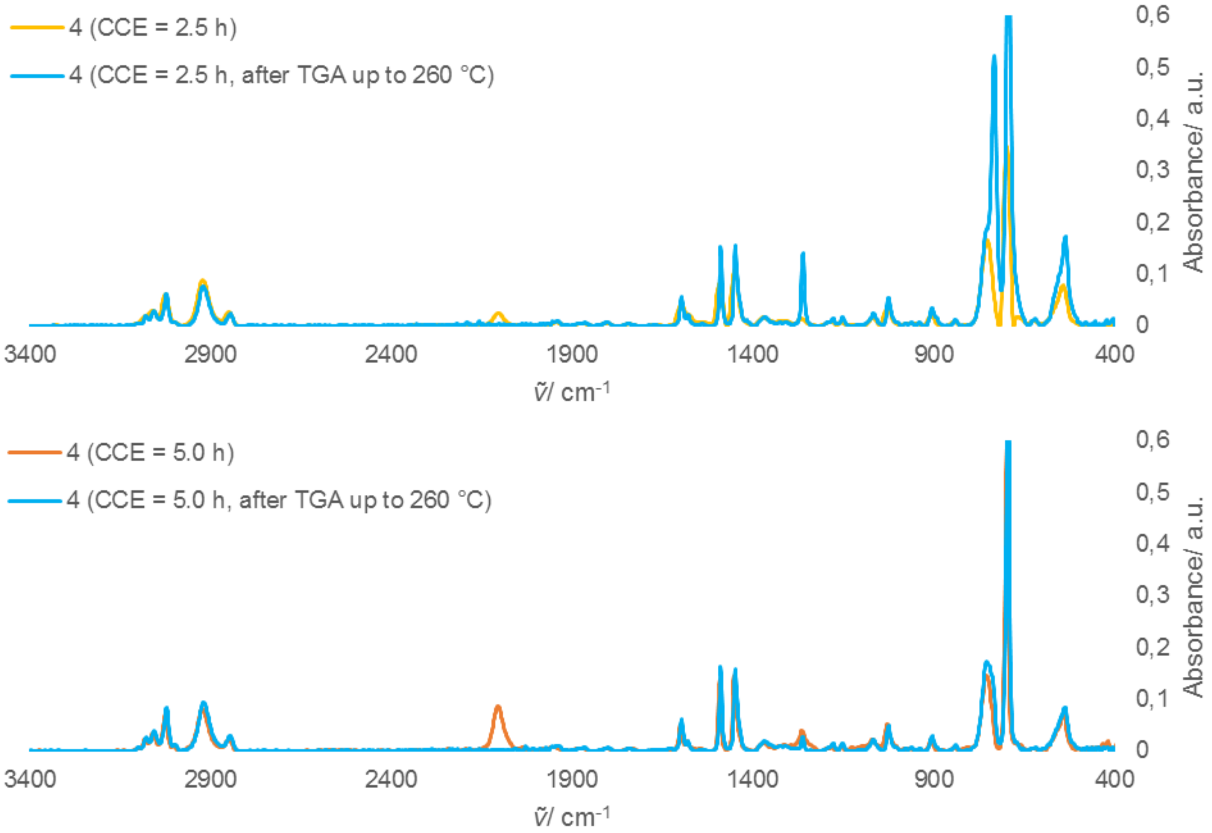


Figure S17. IR spectra of **4** after 2.5 h (top) and 5.0 h (bottom) of CCE.

10.2. Mechanical testing **12** from scale-up

Polymer films (0.04 – 0.10 mm) suitable for static material testing were prepared by evaporation from dichloromethane solution, using styro foam (**SF**, M_w = 248 kDa, $Đ$ = 2.60) and 0.8 mol% functionalized polymer **12** (M_w = 204 kDa, $Đ$ = 2.66). To prepare the solution, 500 mg of sample was dissolved in 10 mL of DCM. Then, the solution was filtered to remove remaining solids and casted on a 4 cm x 4 cm Teflon mold. After evaporation overnight, specimens for analysis were cut into 5 mm x 30 mm test samples. Test specimens were mounted to screw-tight grips (50 N). Tensile stress and strain were measured to the point of break at room temperature at 28 % humidity using an extension speed of 0.2 mm/s with an approximate loading gap of 30 mm on a Zwick testing instruments tension mode. Measurements were repeated for 3 specimens and the Young's modulus *E* was determined by the slope of the elastic deformation of the stress-strain curve. (Table S8).

Table S8: Young's modulus of **12** and parent polymer (SF).

	Polymer	*E*/ MPa
	SF	1195
	SF	1066
	SF	1104
Average *E*/ MPa	SF	1122±54
	12	1067
	12	1075
	12	900
Average *E*/ MPa	12	1014±81

11. Comparison with literature precedents

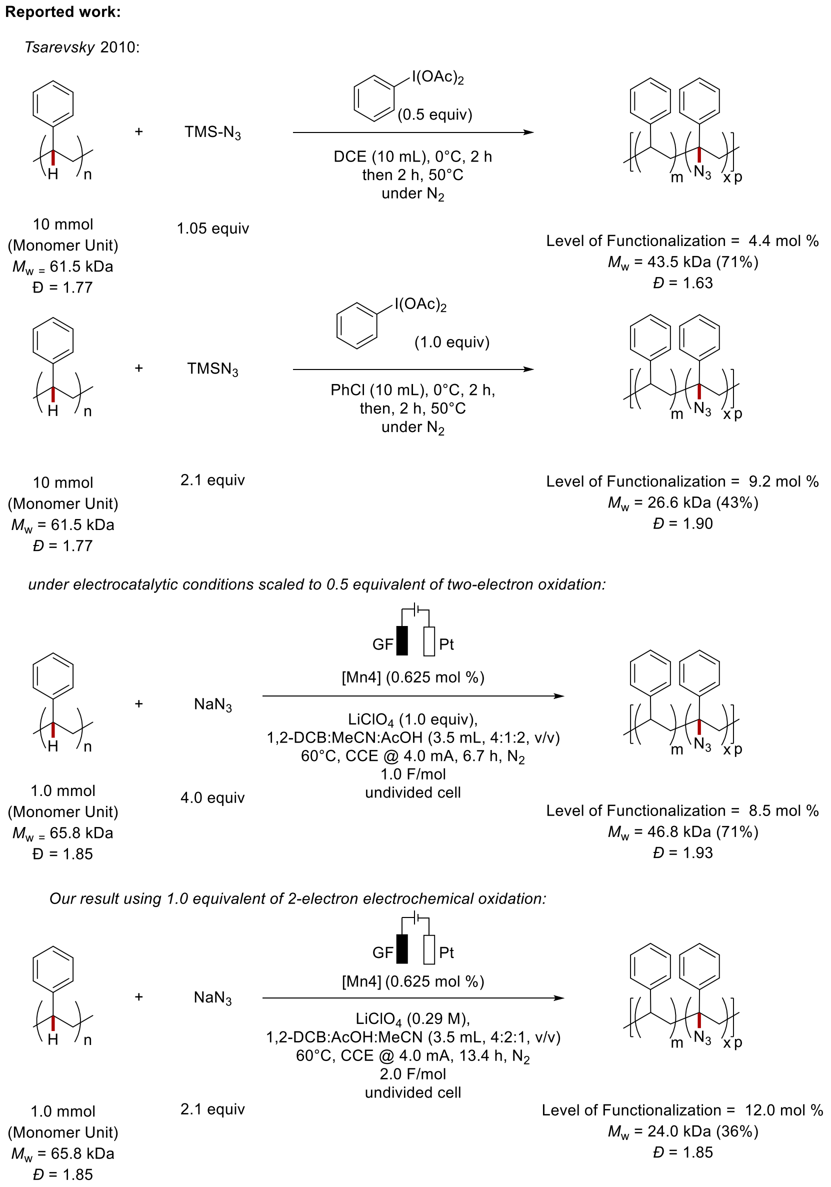


Figure S18. Comparison with literature precedents.[4]

The level of functionalization was determined using an IR-^{1}H NMR correlation curve (m = 2.7051 mol %, R^2=0.9942) and the relative IR intensity of the N_3-Band (2106 cm^{-1}) to the benzylic C–H band (3026 cm^{-1}) of the polystyrene sample. The mass average molar mass and polymer dispersity were determined by GPC against narrow-disperse polystyrene standards using THF as eluent at 30 °C and were reported as the molar weight retention of the parent polymer in parenthesis.

12. Characterization Data

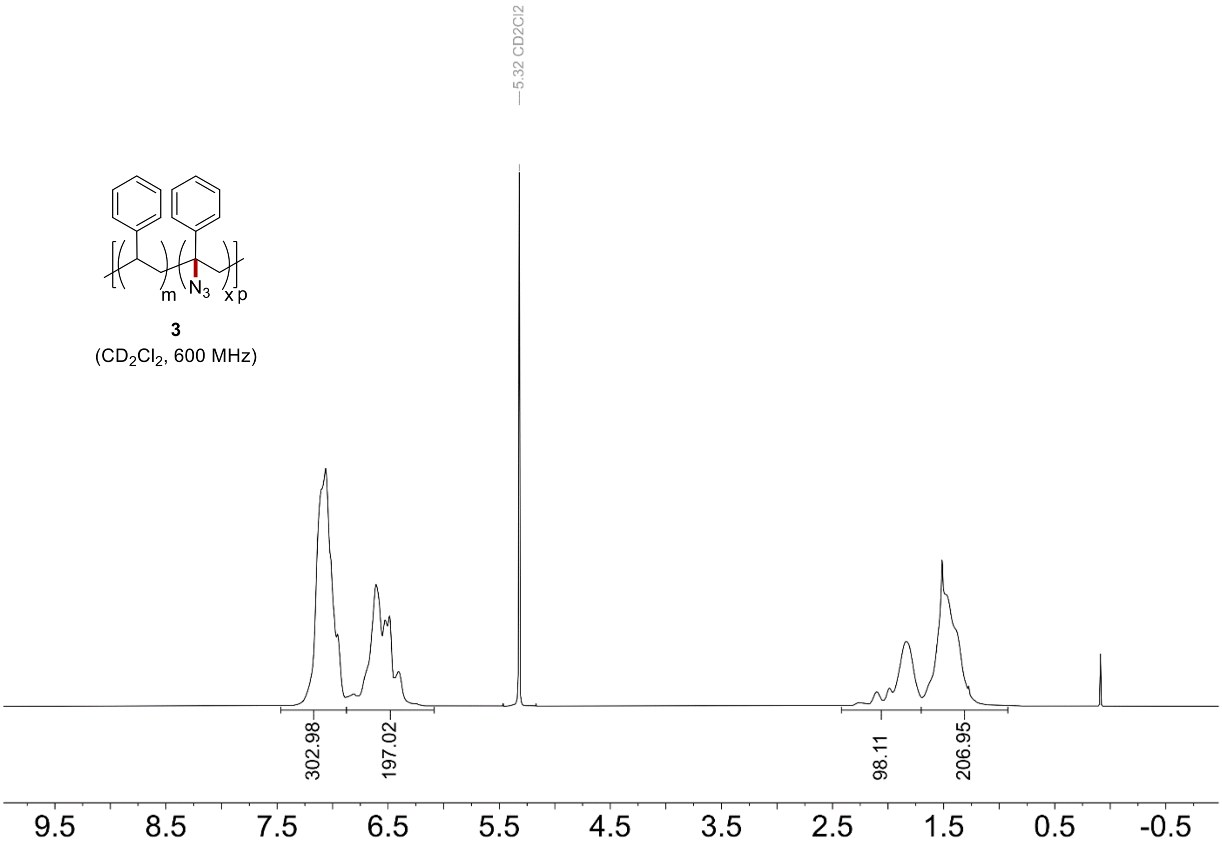


Figure S19. ^{1}H NMR of **3** in CD_2Cl_2.

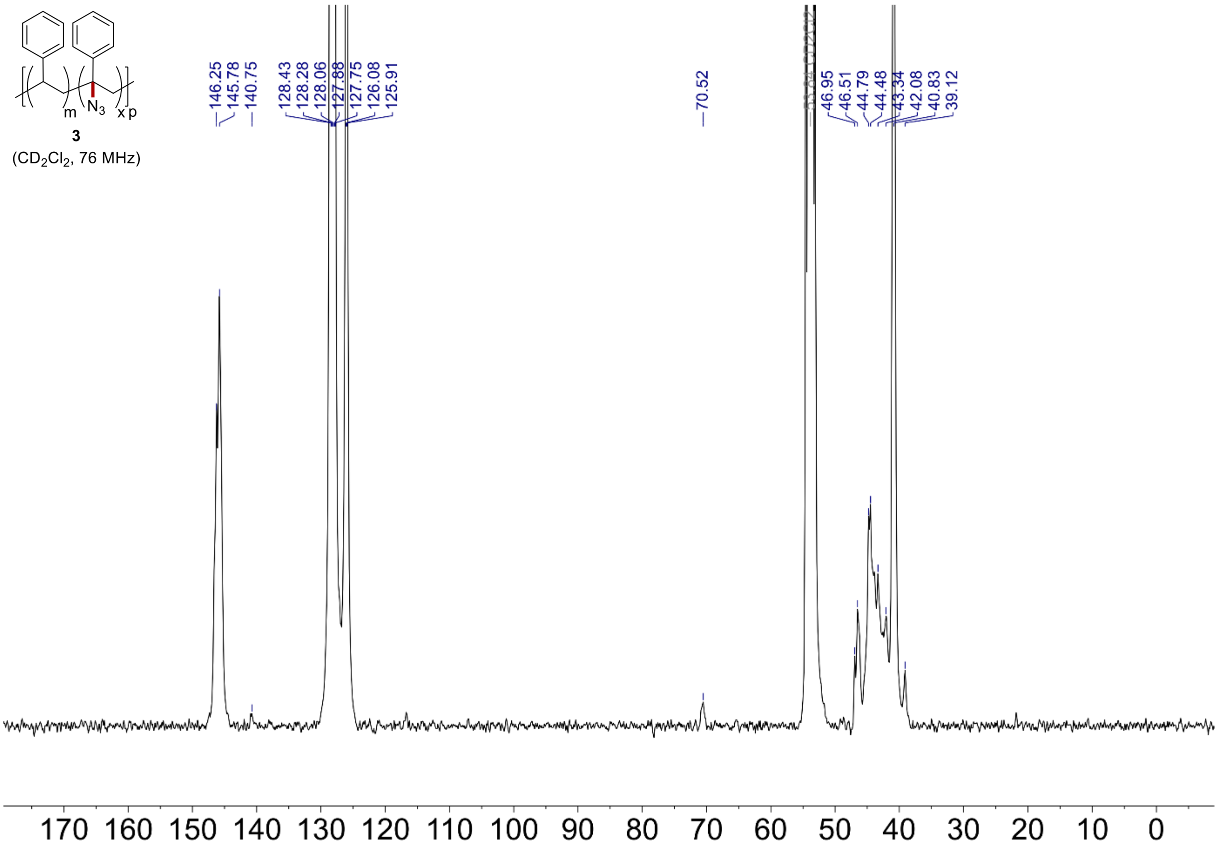


Figure S20. ^{13}C NMR of **3** in CD_2Cl_2.

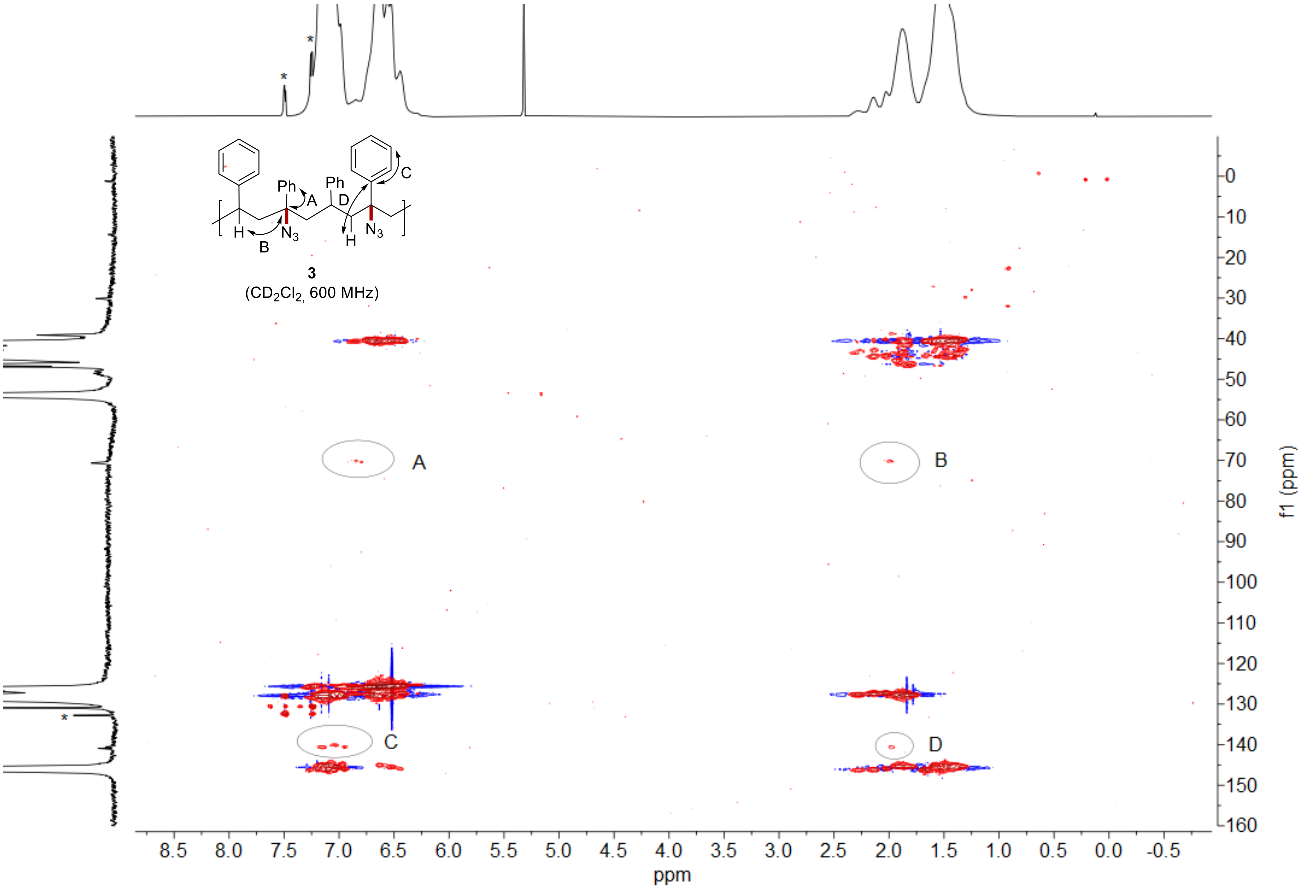


Figure S21. HMBC of **3** in CD_2Cl_2. Asterisk marks 1,2-DCB impurities.

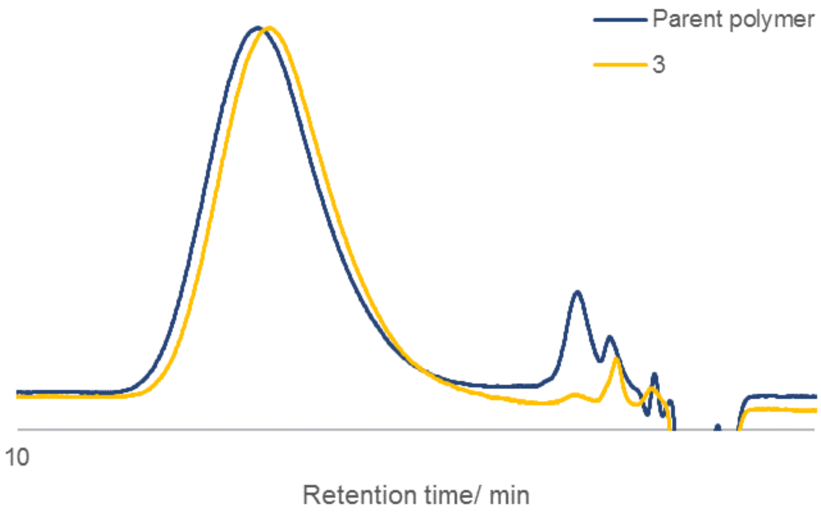


Figure S22. Normalized chromatogram of parent (blue) and modified polymer **3** (yellow).

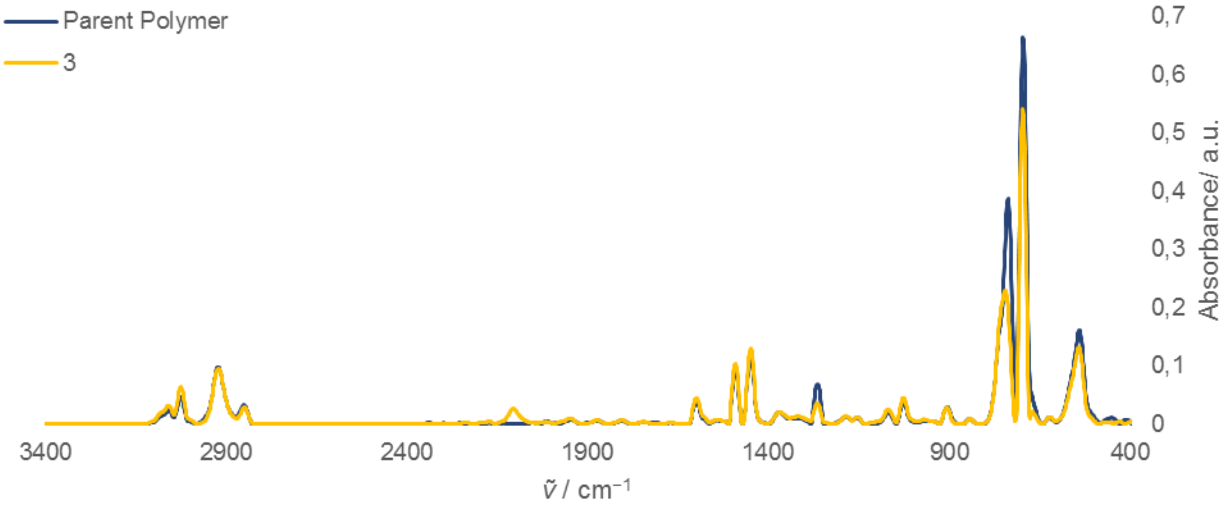


Figure S23. IR spectrum of parent (blue) and modified polymer **3** (yellow) in arbitrary units (a.u.).

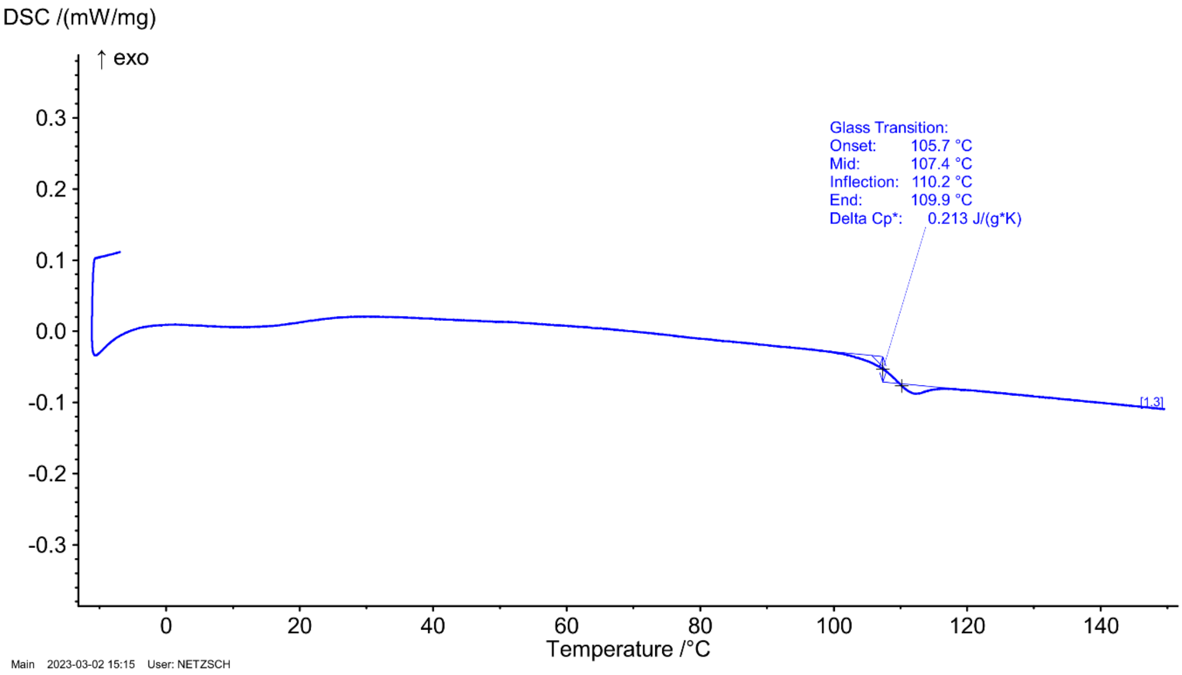


Figure S24. DSC of **3**.

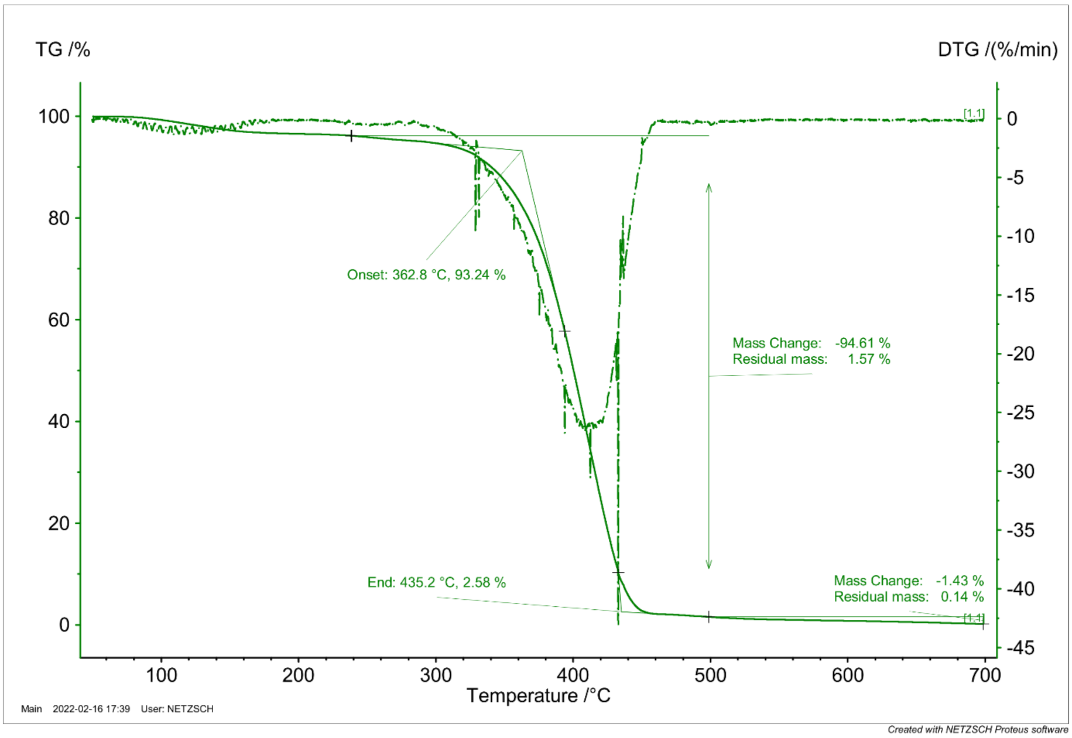


Figure S25. TGA of **3**.

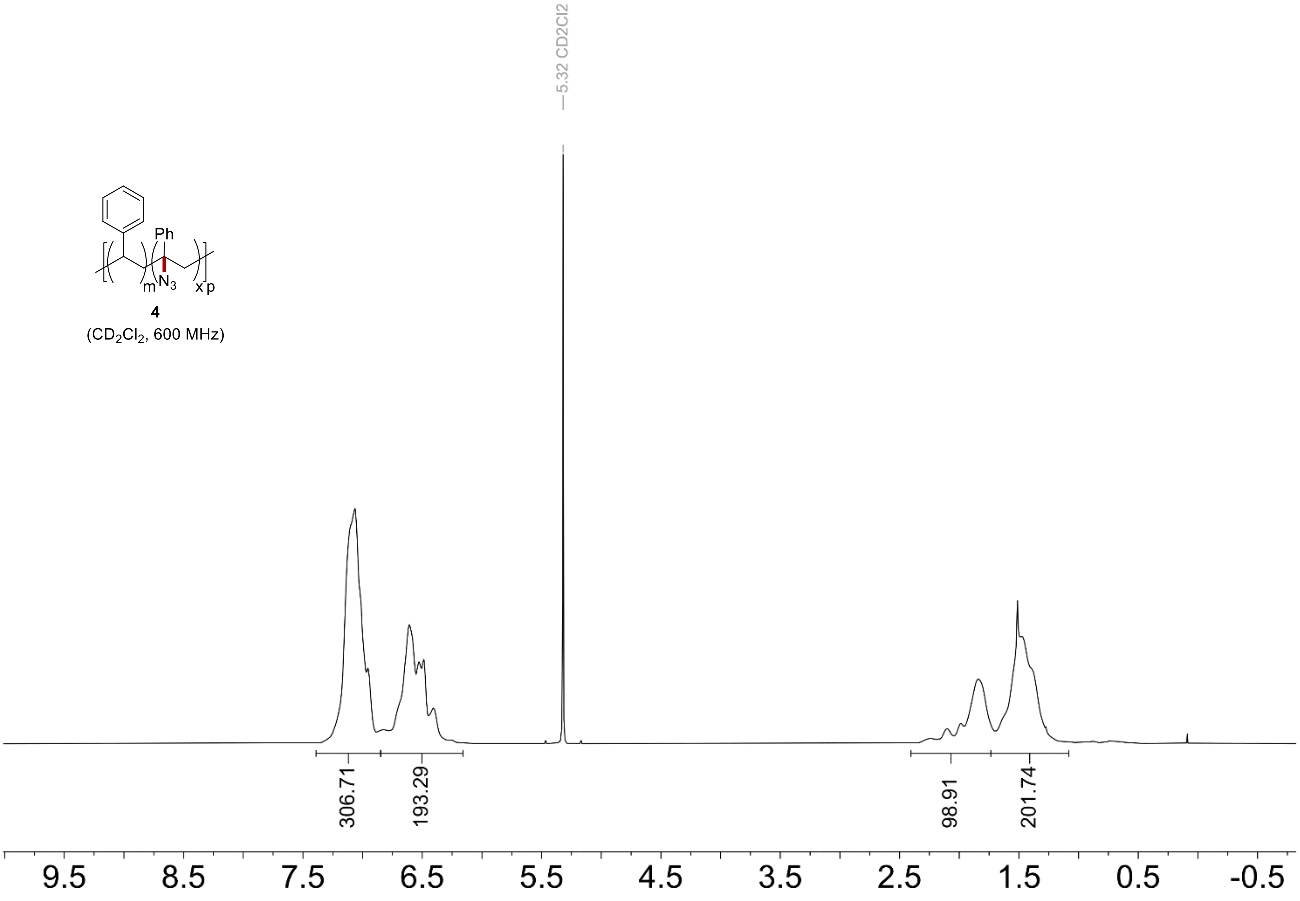


Figure S26. ^{1}H NMR of **4** in CD$_2$Cl$_2$.

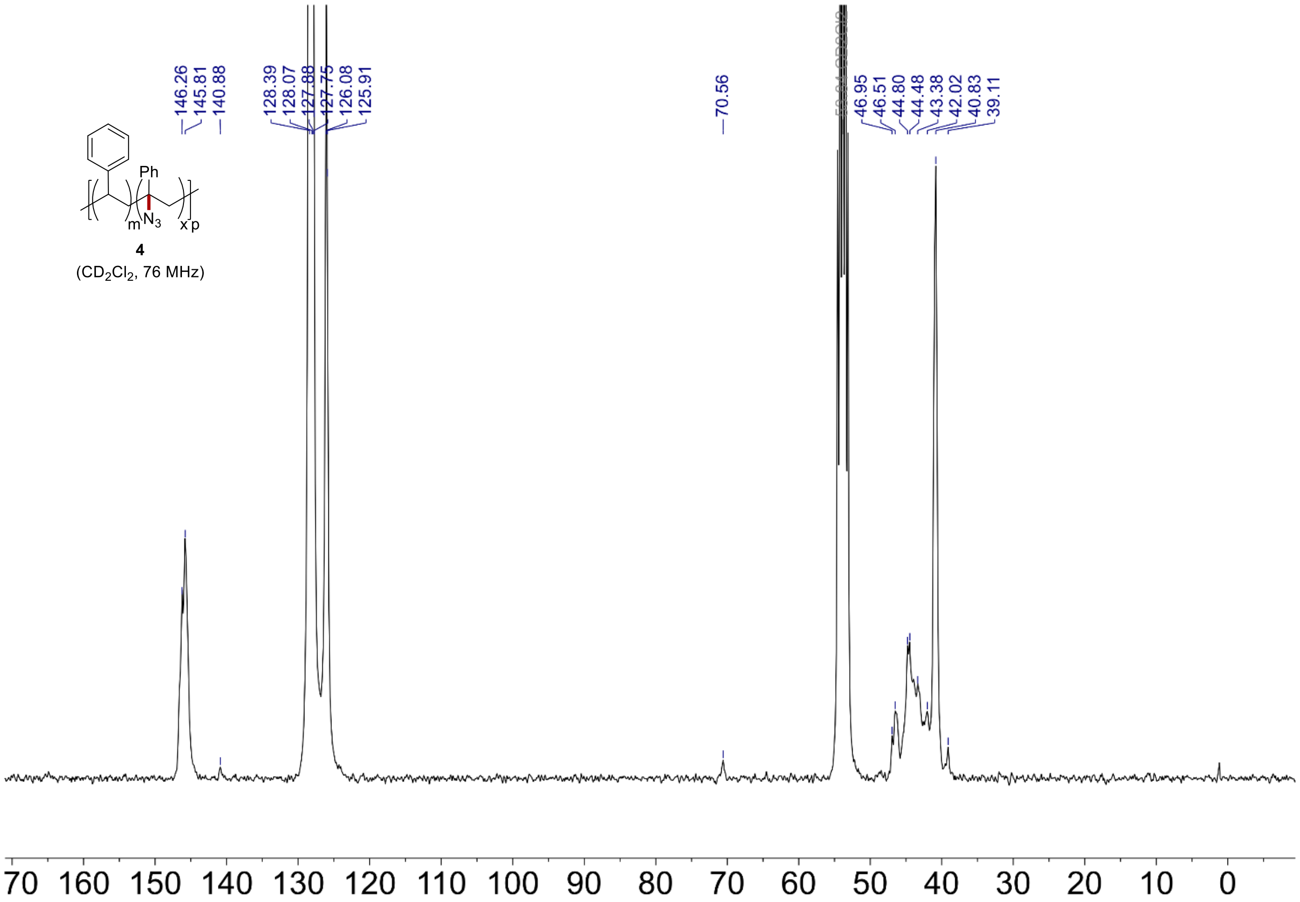


Figure S27. ^{13}C NMR of **4** in CD_2Cl_2.

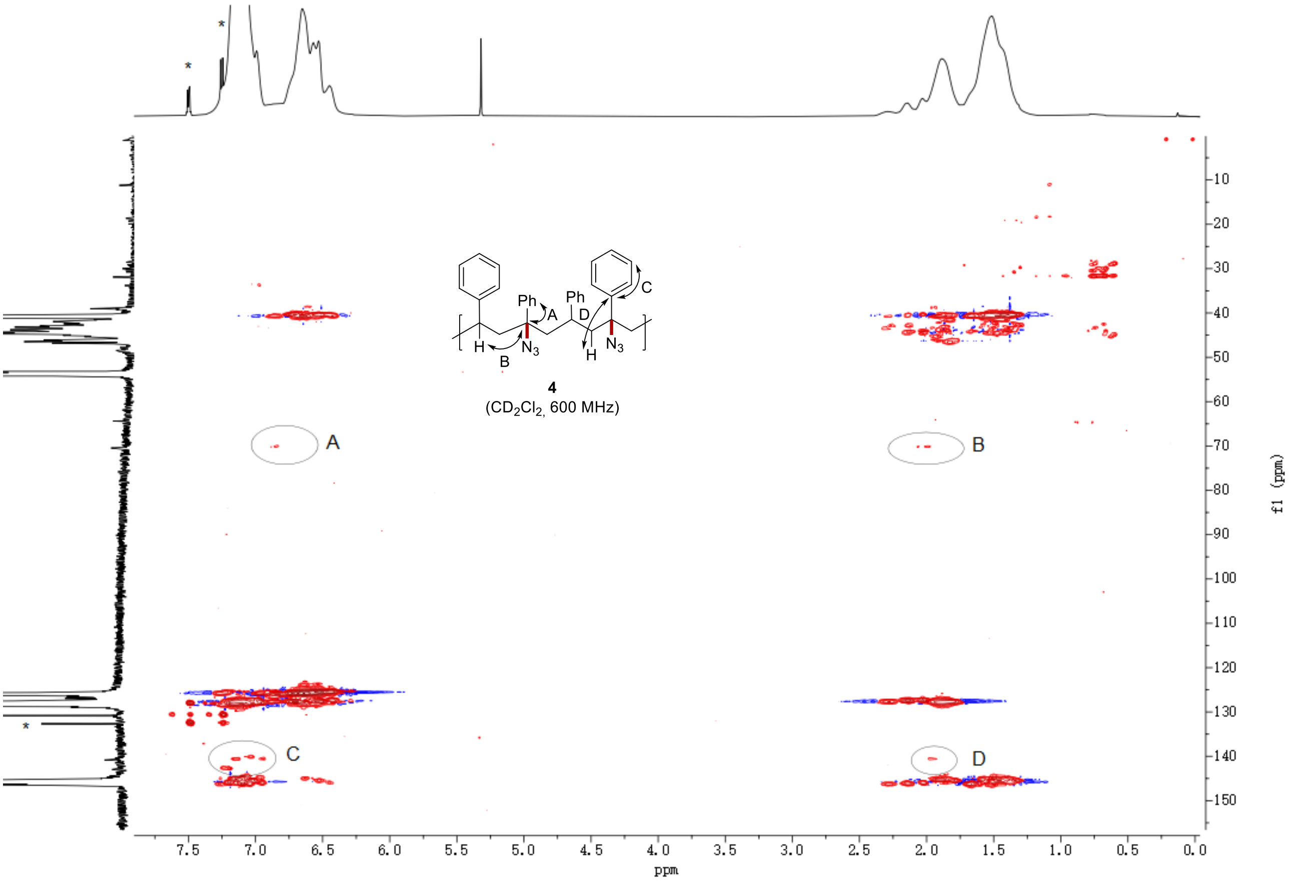


Figure S28. HMBC of **4** in CD_2Cl_2. Asterisk marks 1,2-DCB impurities.

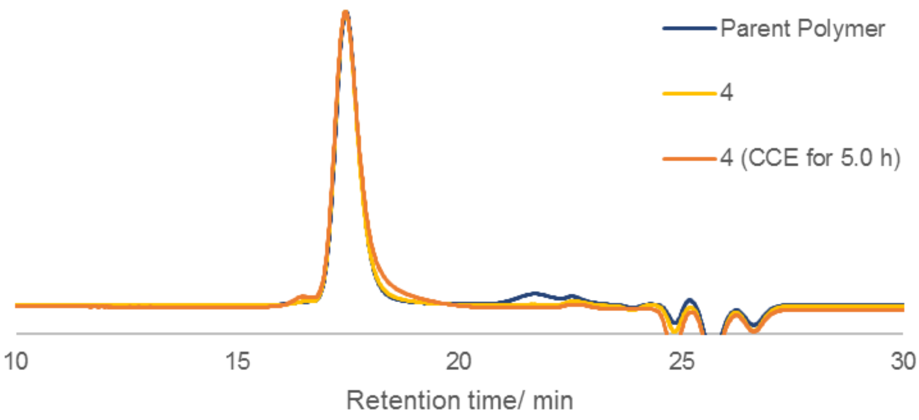


Figure S29. Normalized chromatogram of parent (blue), modified polymer **4** after 2.5 h (yellow) and 5.0 h of CCE (orange).

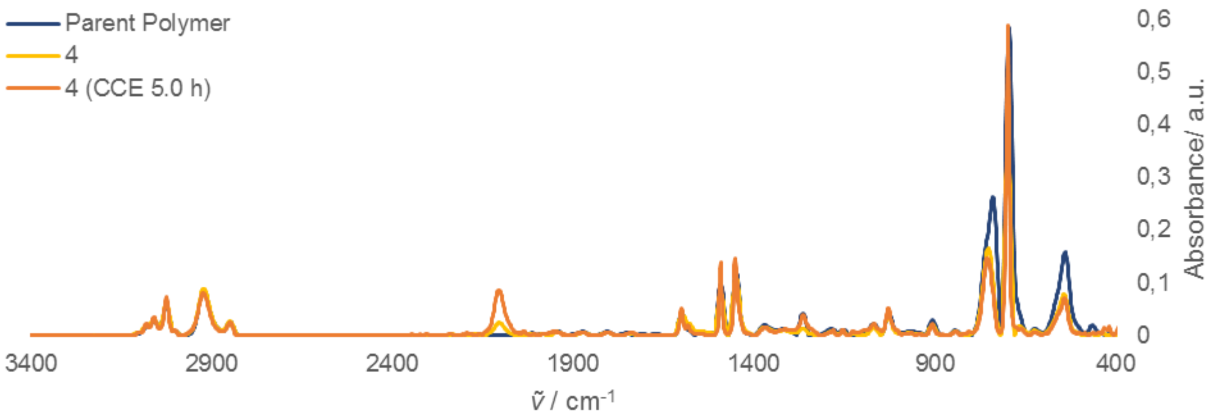


Figure S30. IR spectrum of parent (blue) and modified polymer **4** after 2.5 h (yellow) and 5.0 h of CCE (orange) in arbitrary units (a.u.).

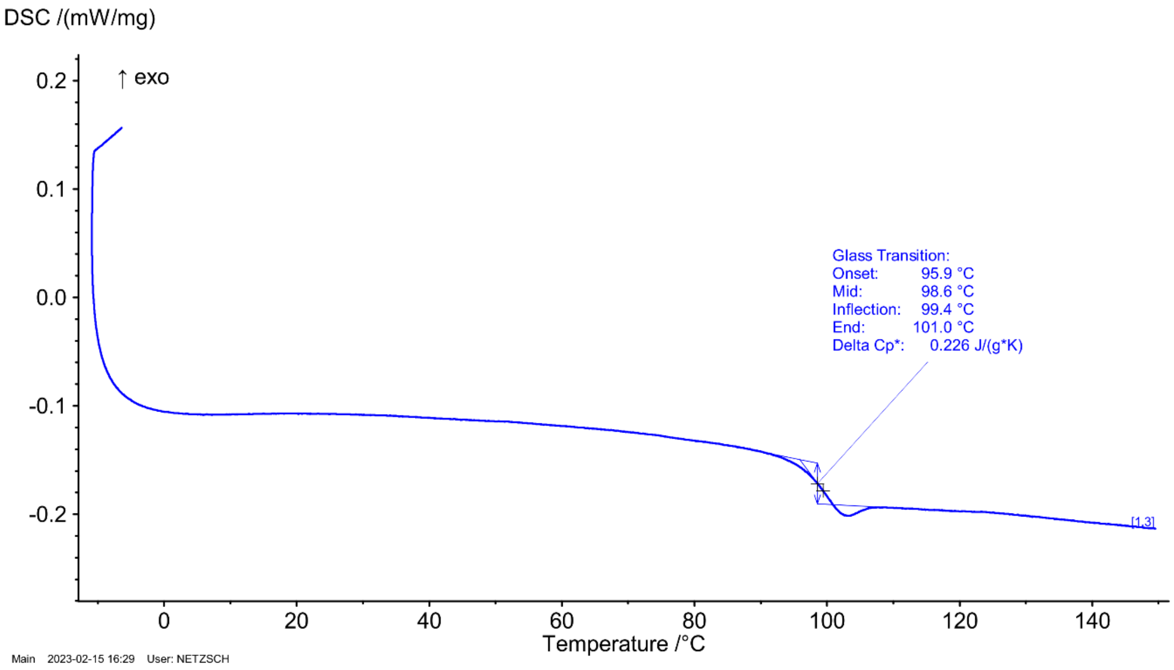


Figure S31. DSC of **4** (CCE = 2.5 h).

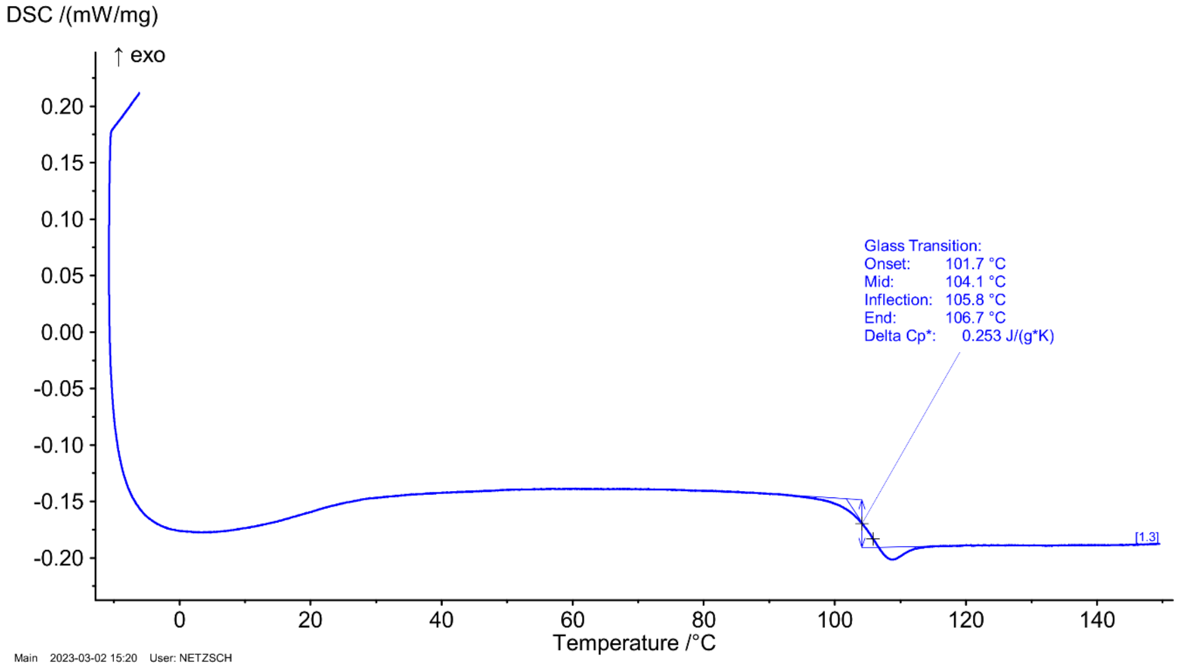


Figure S32. DSC of **4** (CCE = 5.0 h).

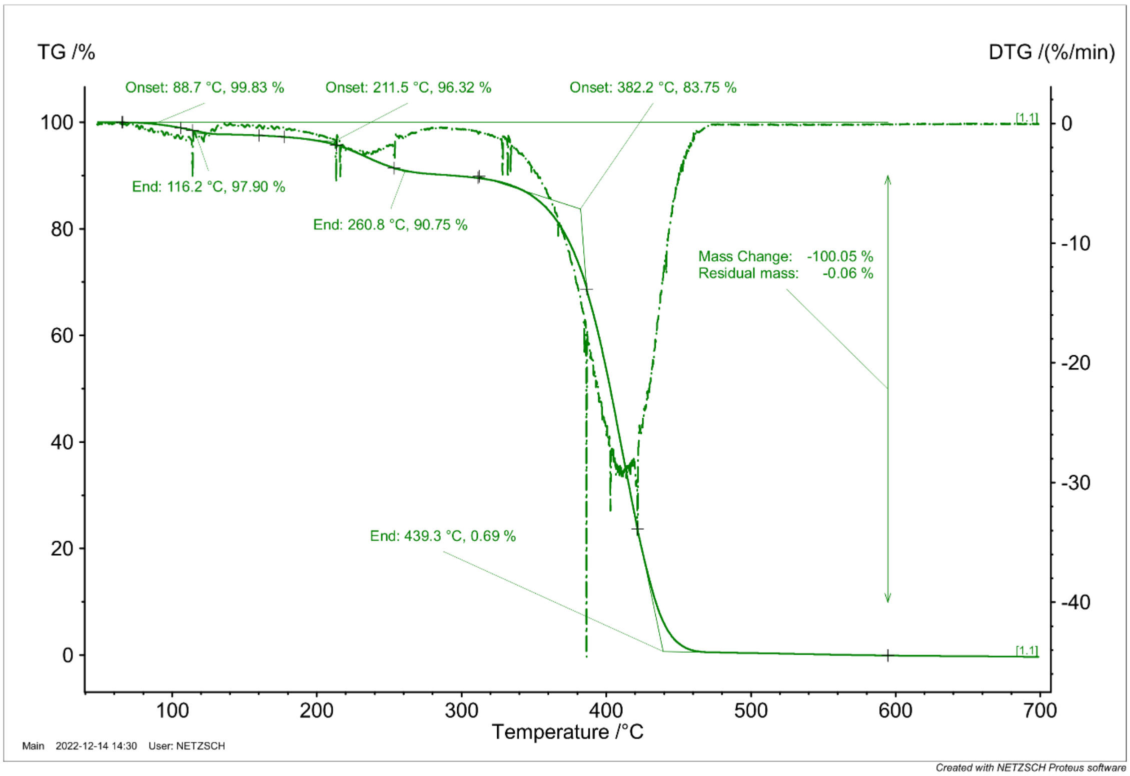


Figure S33. TGA of **4** (CCE = 2.5 h).

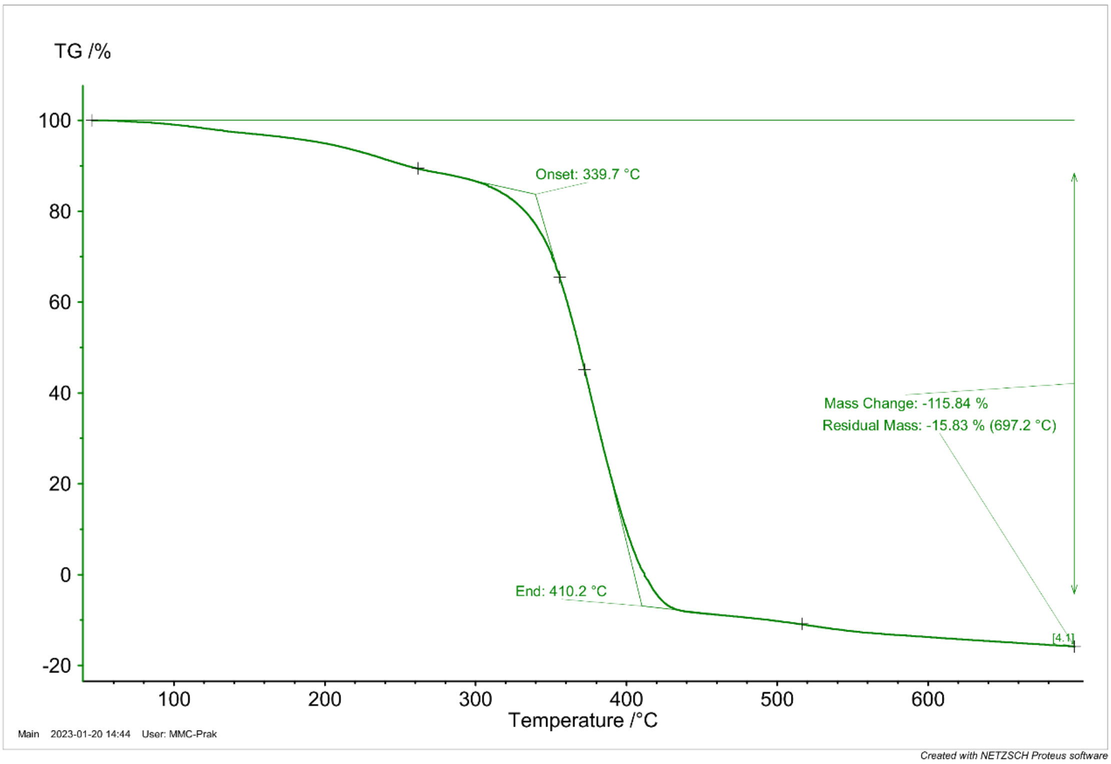


Figure S34. TGA of **4** (CCE = 5.0 h).

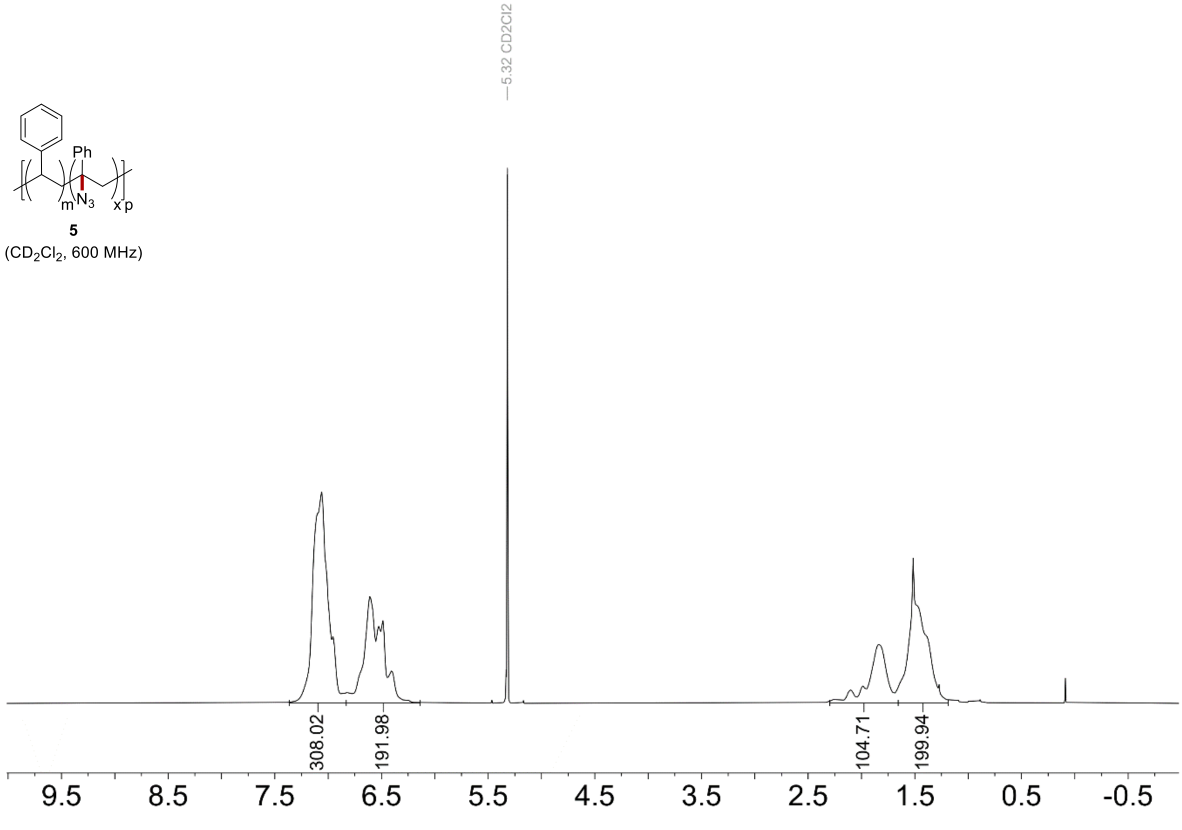


Figure S35. ^{1}H NMR of **5** in CD_2Cl_2.

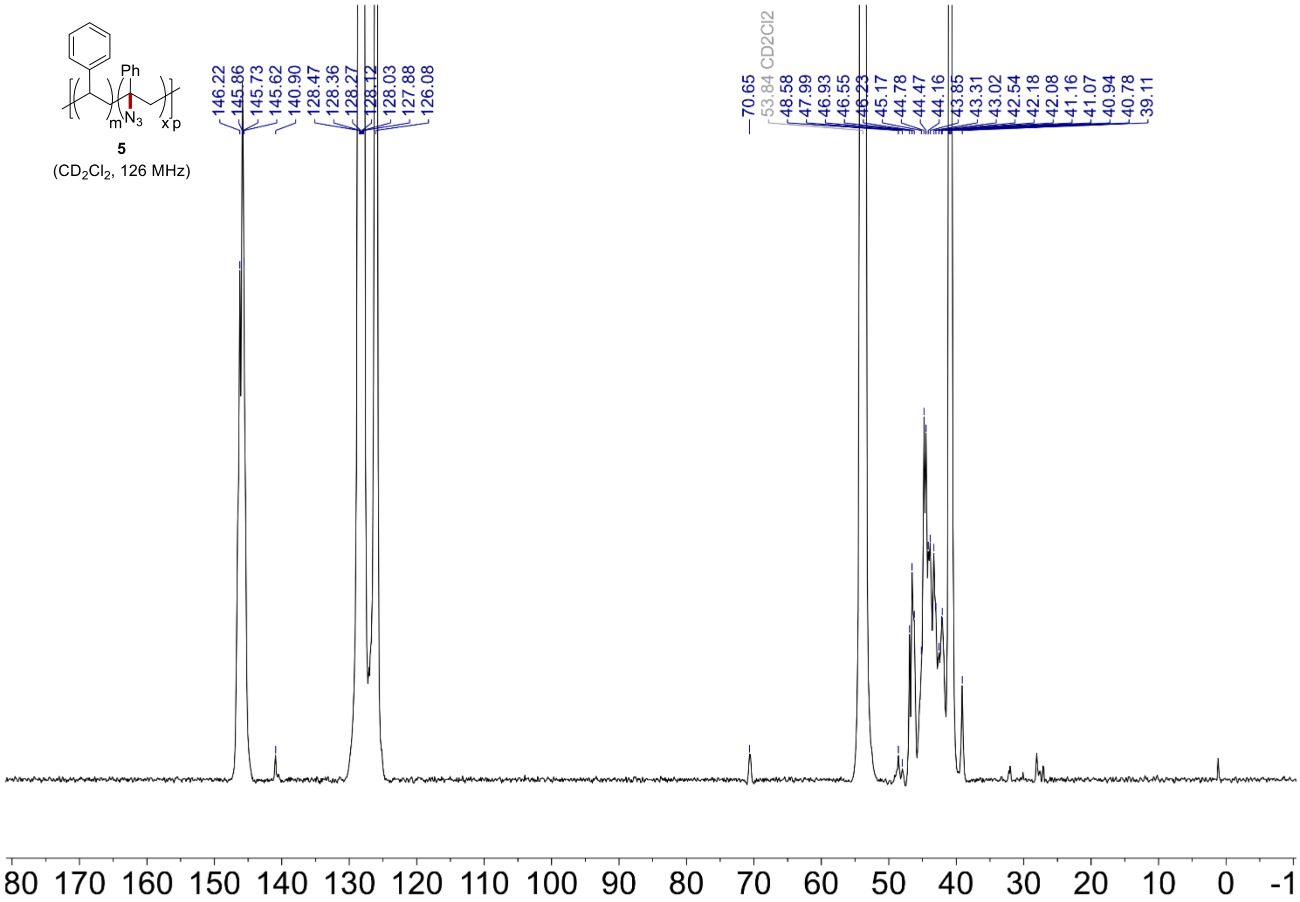


Figure S36. ^{13}C NMR of **5** in CD_2Cl_2.

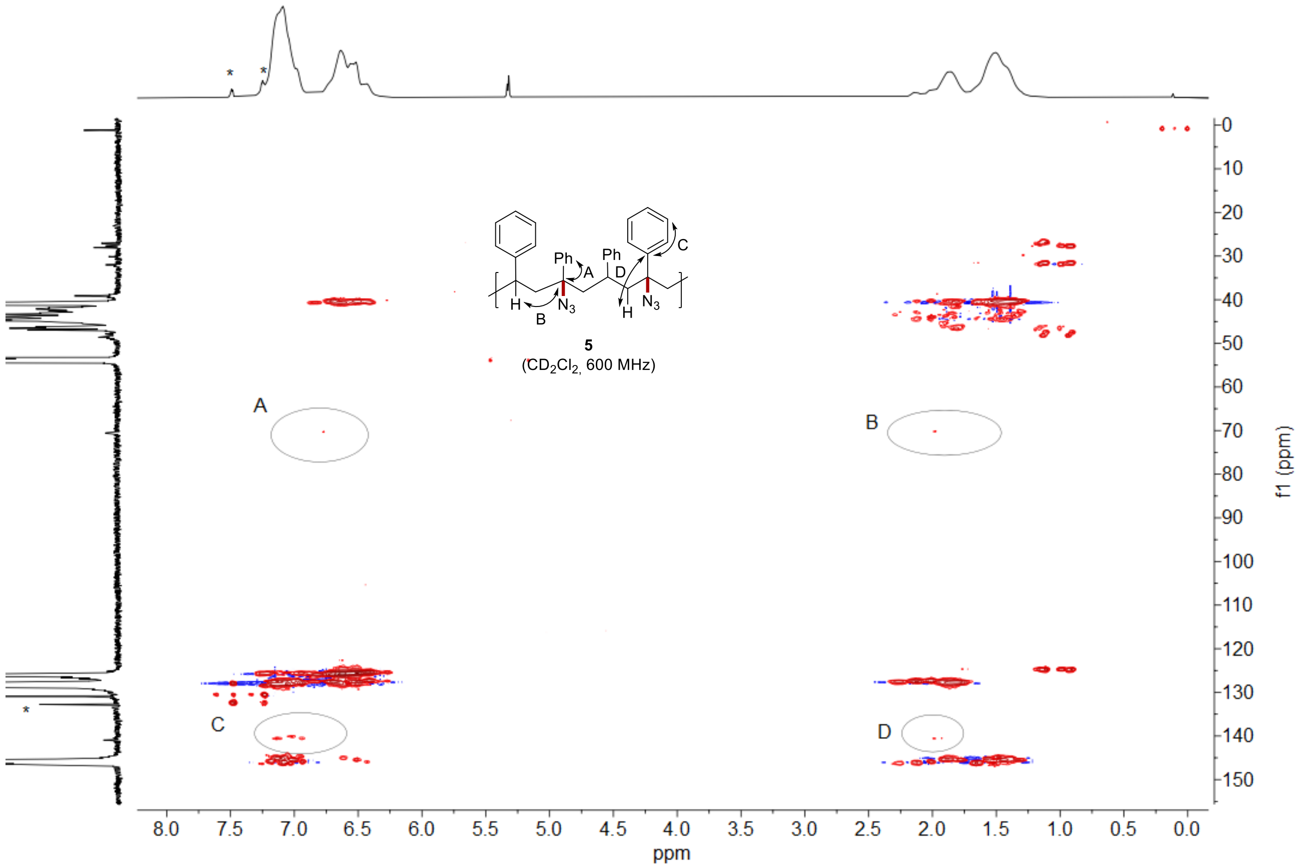


Figure S37. HMBC of **5** in CD_2Cl_2. Asterisk marks 1,2-DCB impurities**.**

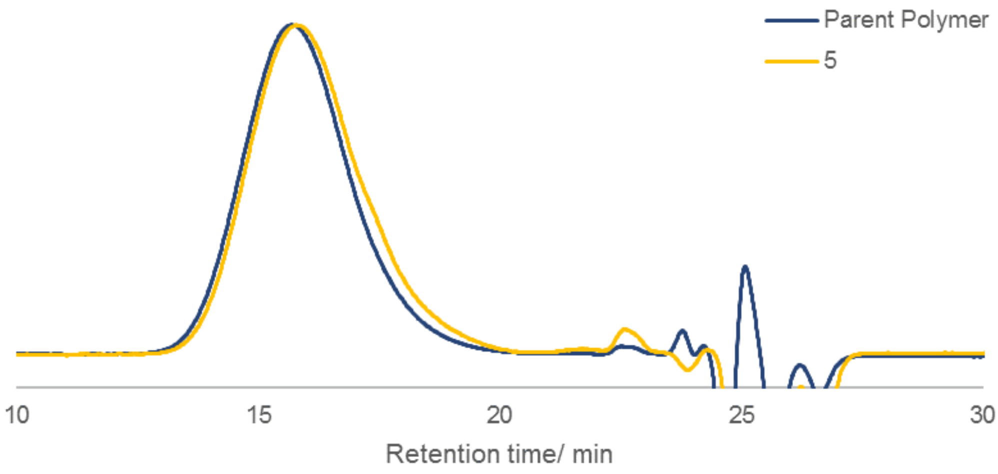


Figure S38. Normalized chromatogram of parent (blue) and modified polymer **5** (yellow).

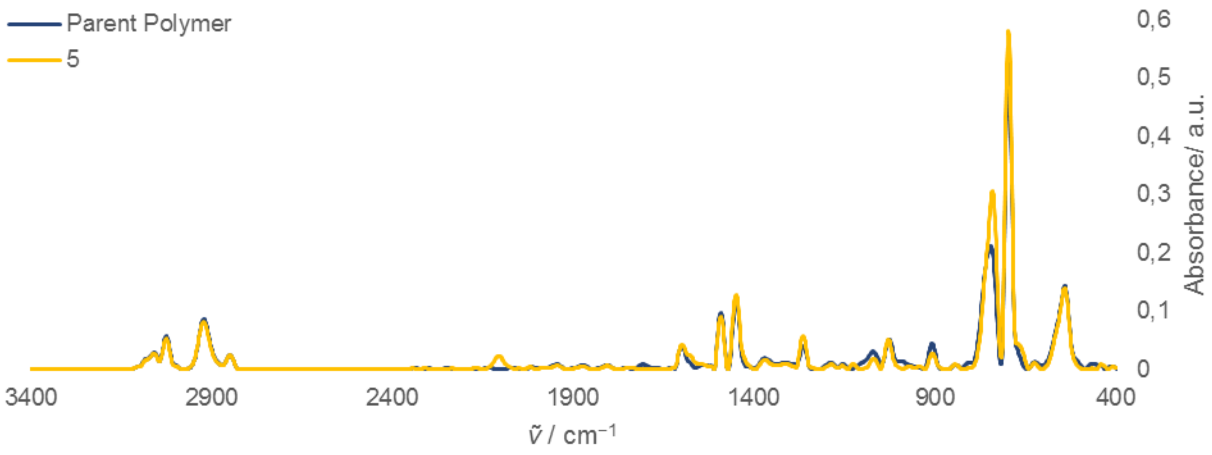


Figure S39. IR spectrum of parent (blue) and modified polymer **5** (yellow) in arbitrary units (a.u.).

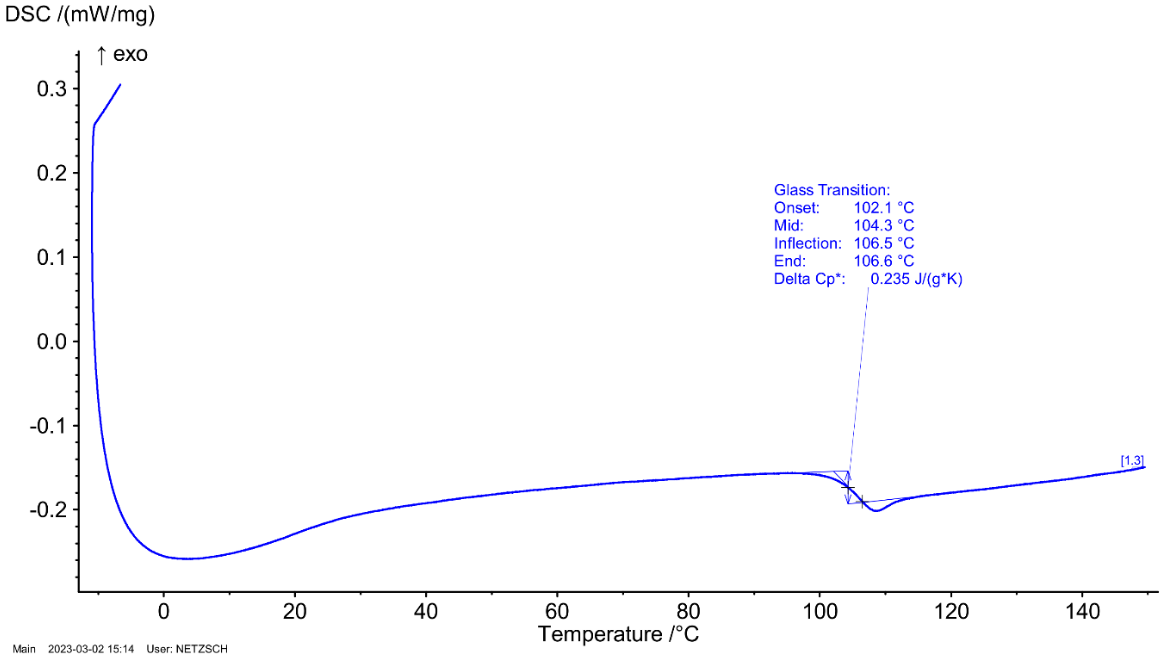


Figure S40. DSC of **5**.

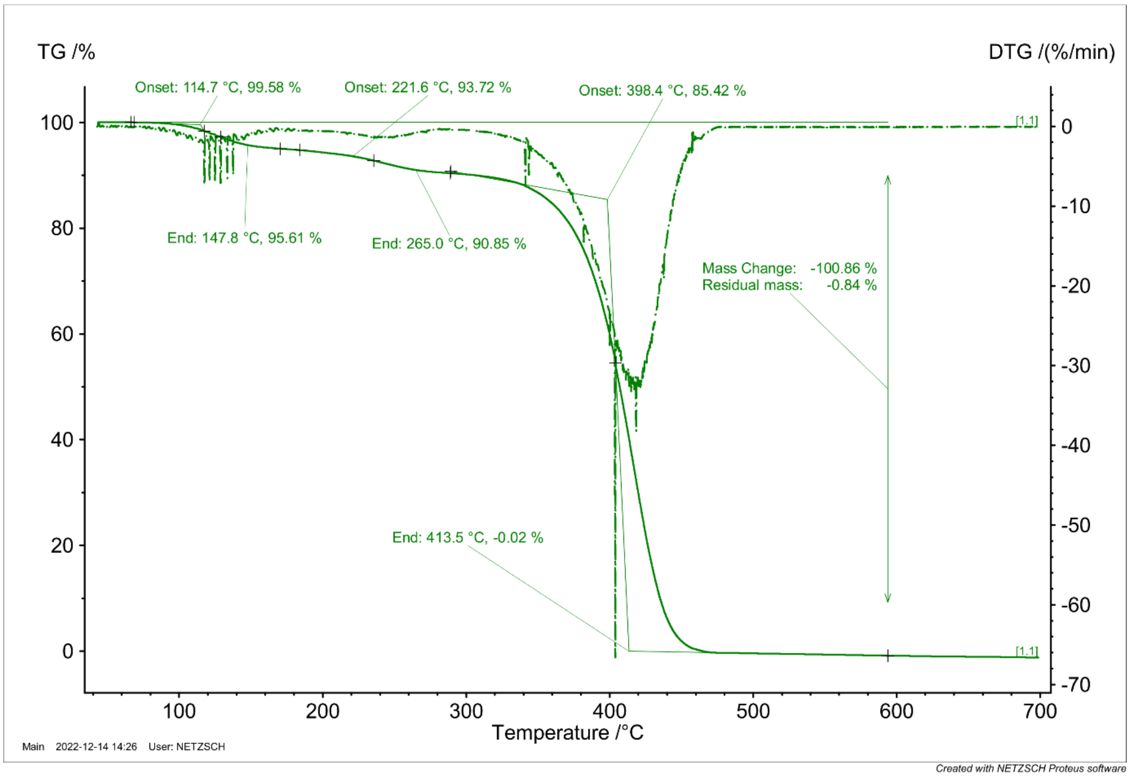


Figure S41. TGA of **5**.

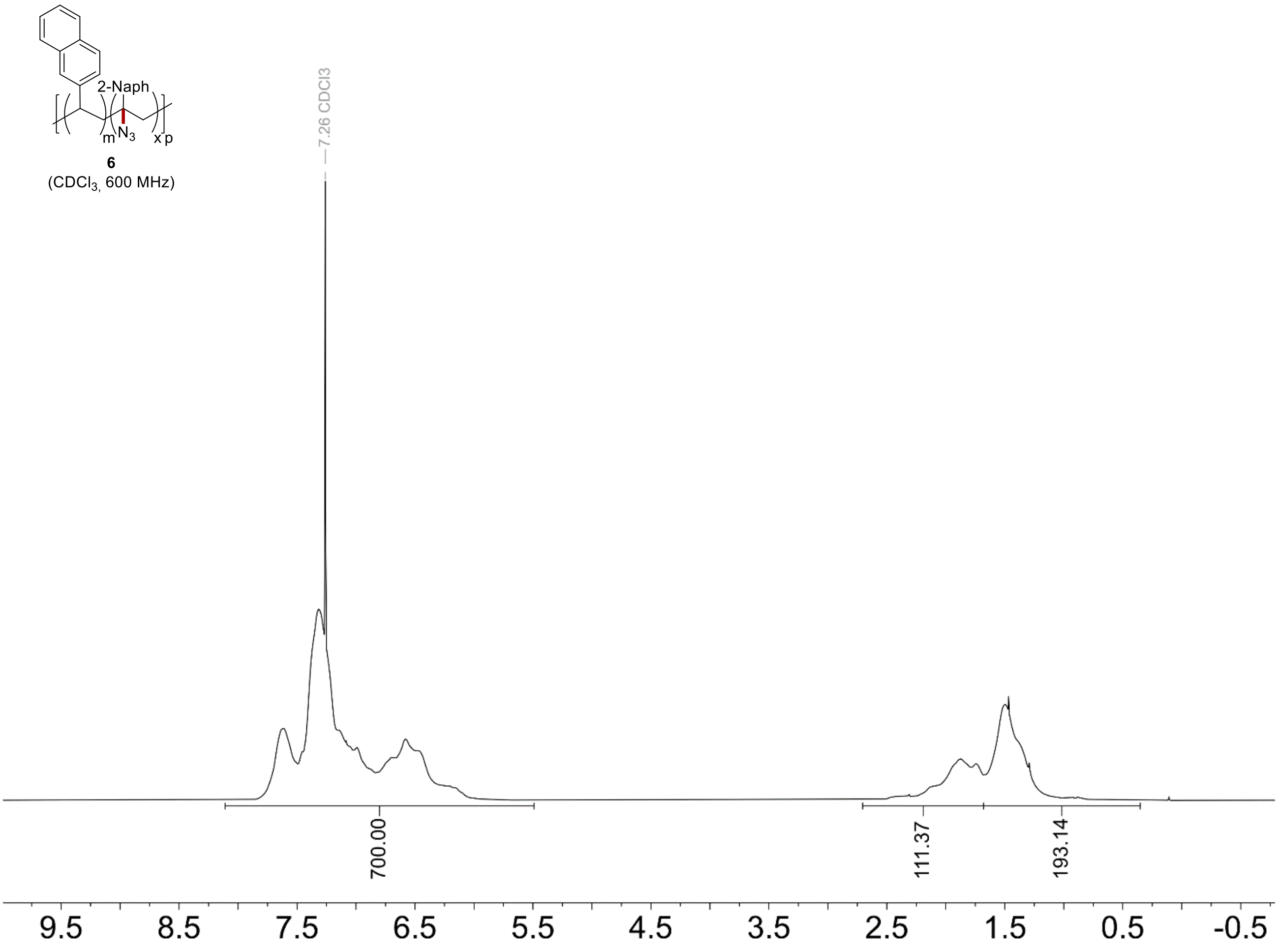


Figure S42. ^{1}H NMR of **6** in $CDCl_3$.

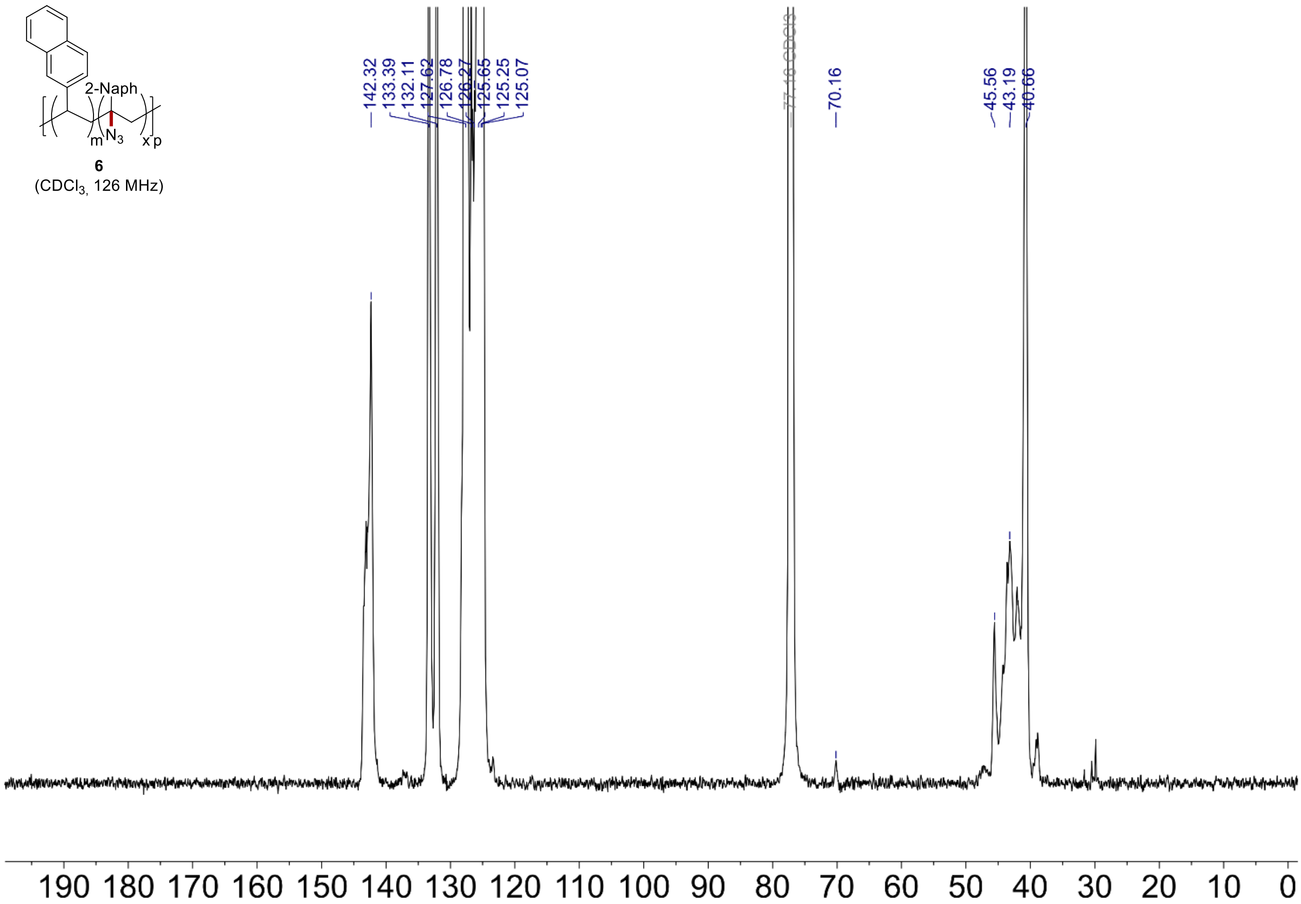


Figure S43. ^{13}C NMR of **6** in CDCl$_3$.

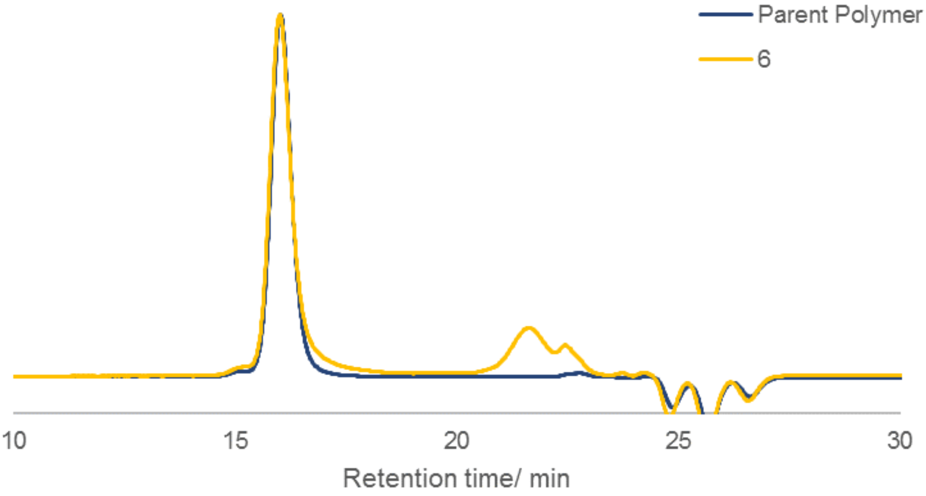


Figure S44. Normalized chromatogram of parent (blue) and modified polymer **6** (yellow).

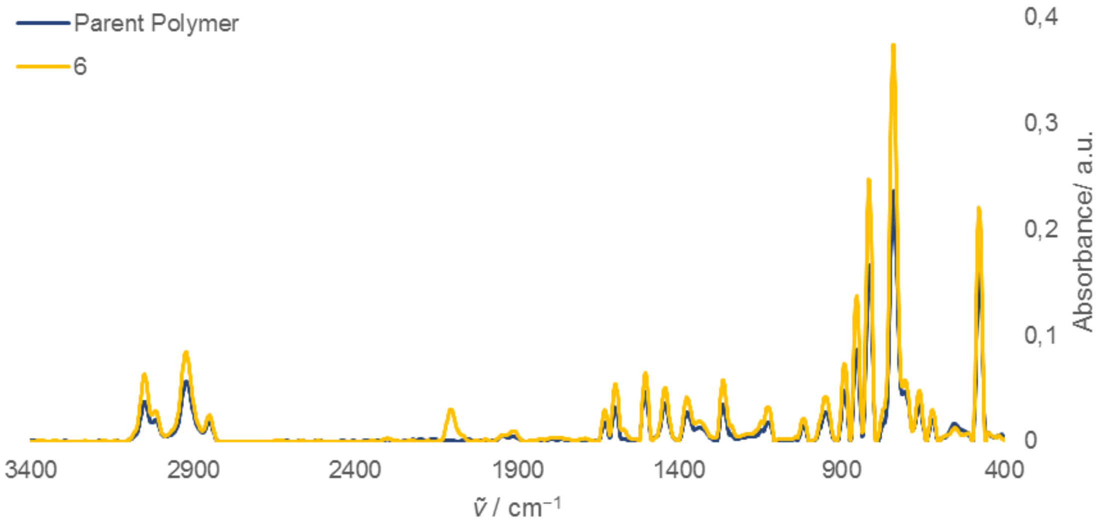


Figure S45. IR spectrum of parent (blue) and modified polymer **6** (yellow) in arbitrary units (a.u.).

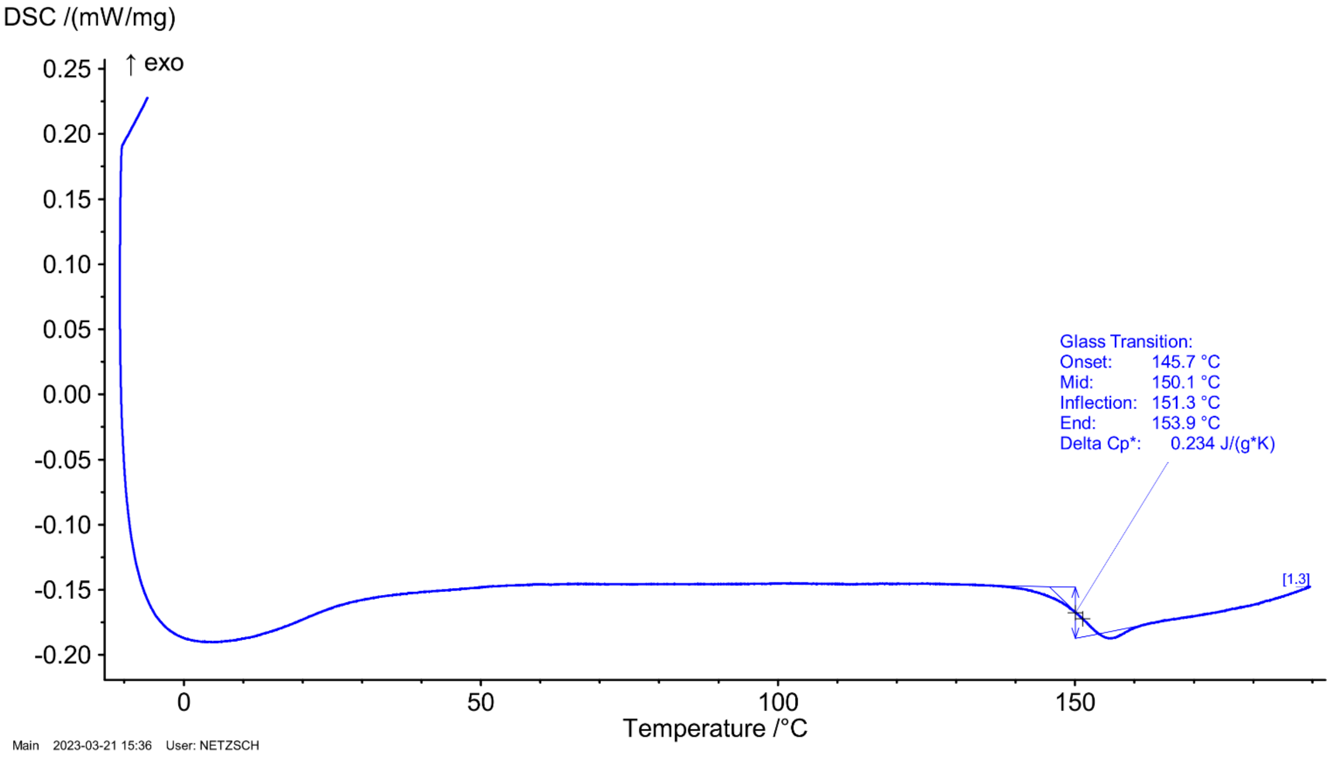


Figure S46. DSC of **6**.

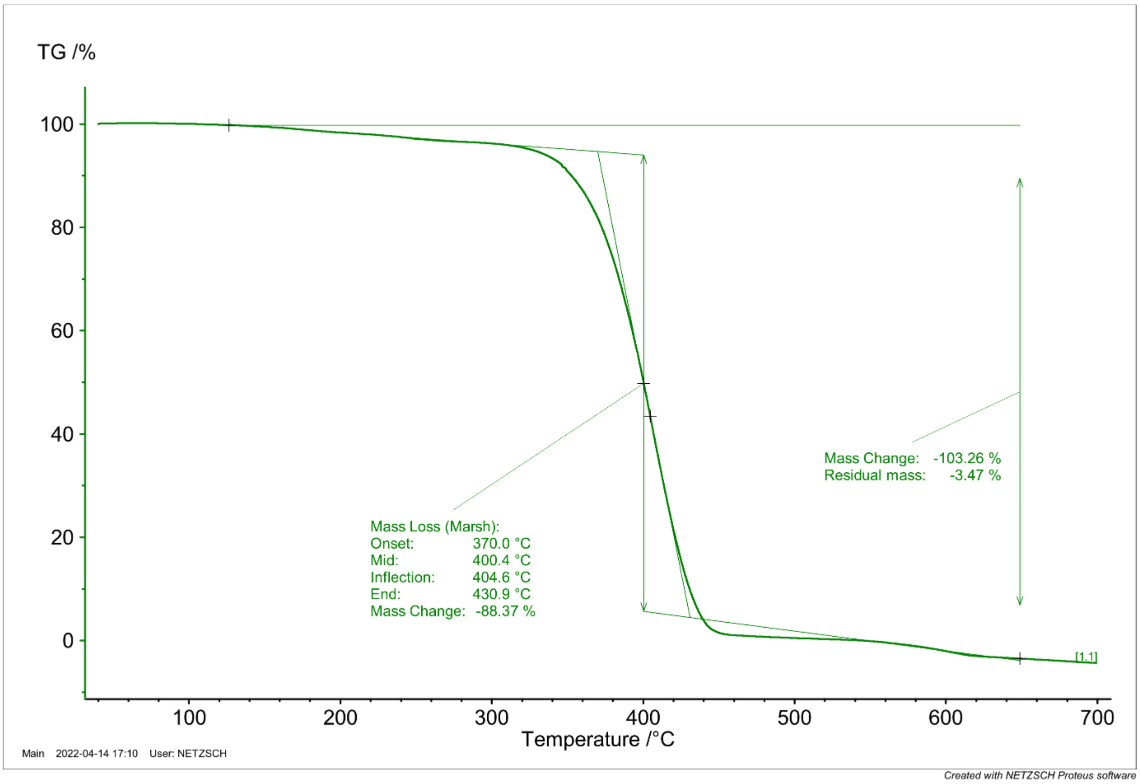


Figure S47. TGA of **6**.

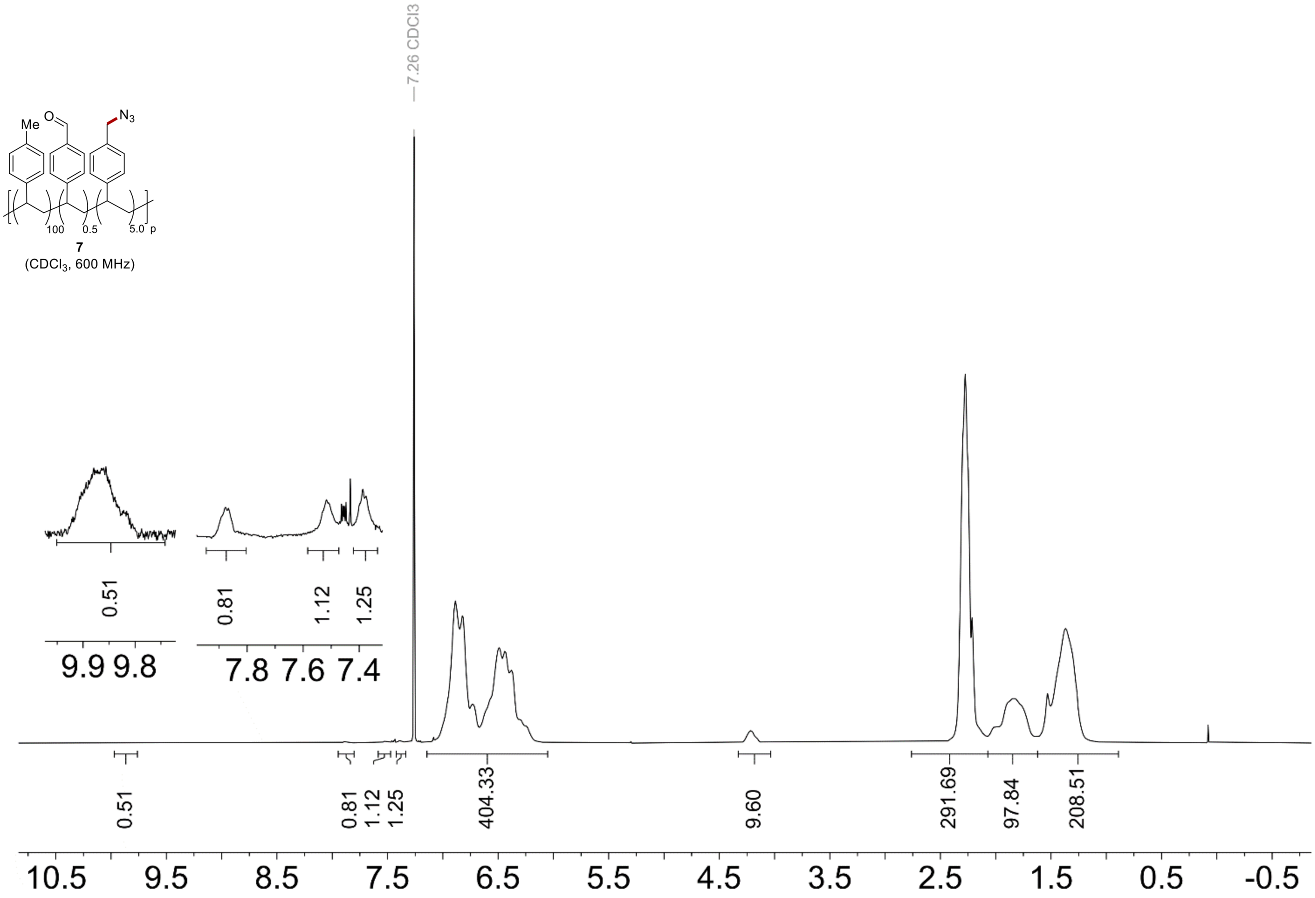


Figure S48. ^{1}H NMR of **7** in $CDCl_3$.

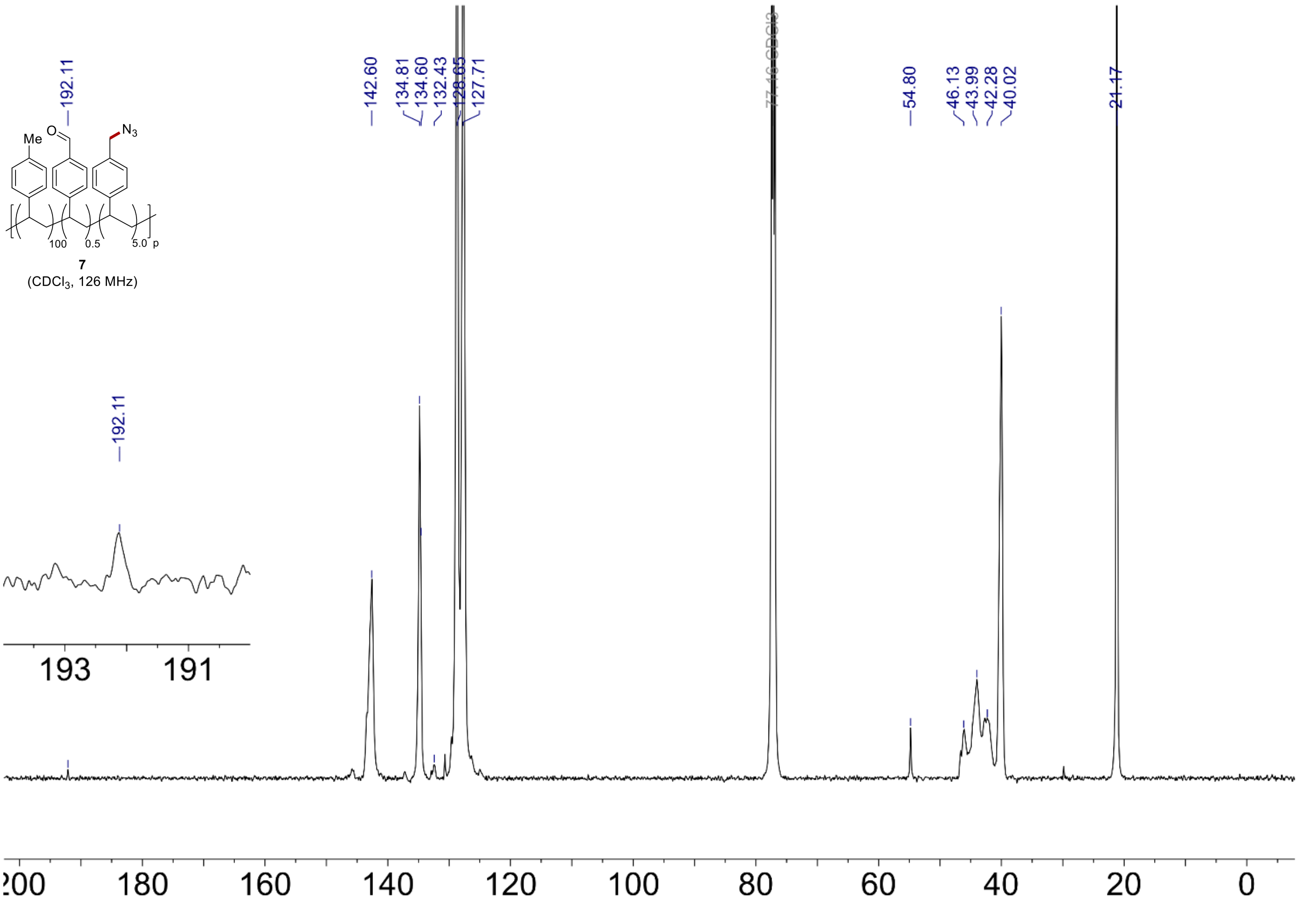


Figure S49. ^{13}C NMR of **7** in CDCl$_3$.

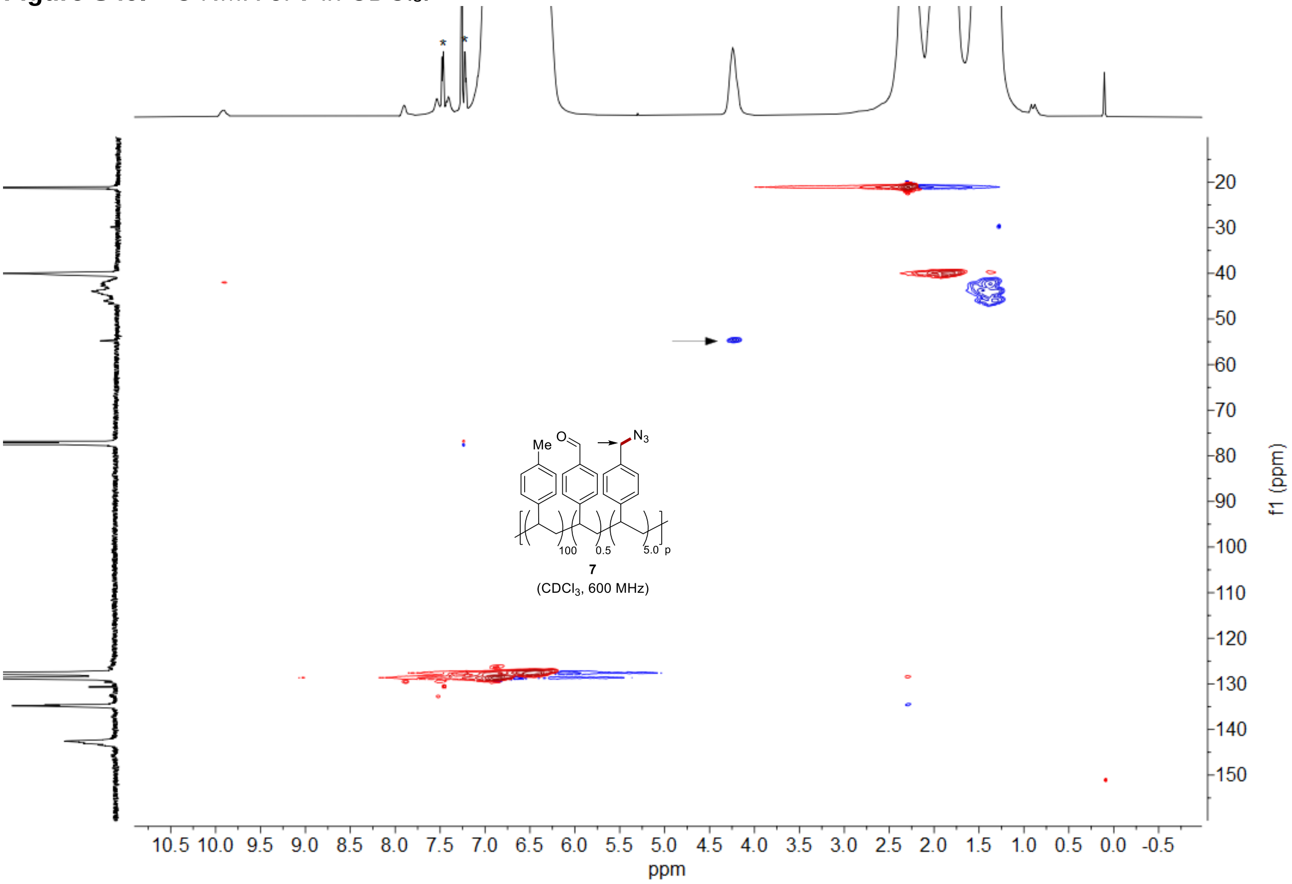


Figure S50. HSQC of **7** in CDCl$_3$. Asterisk marks 1,2-DCB impurities.

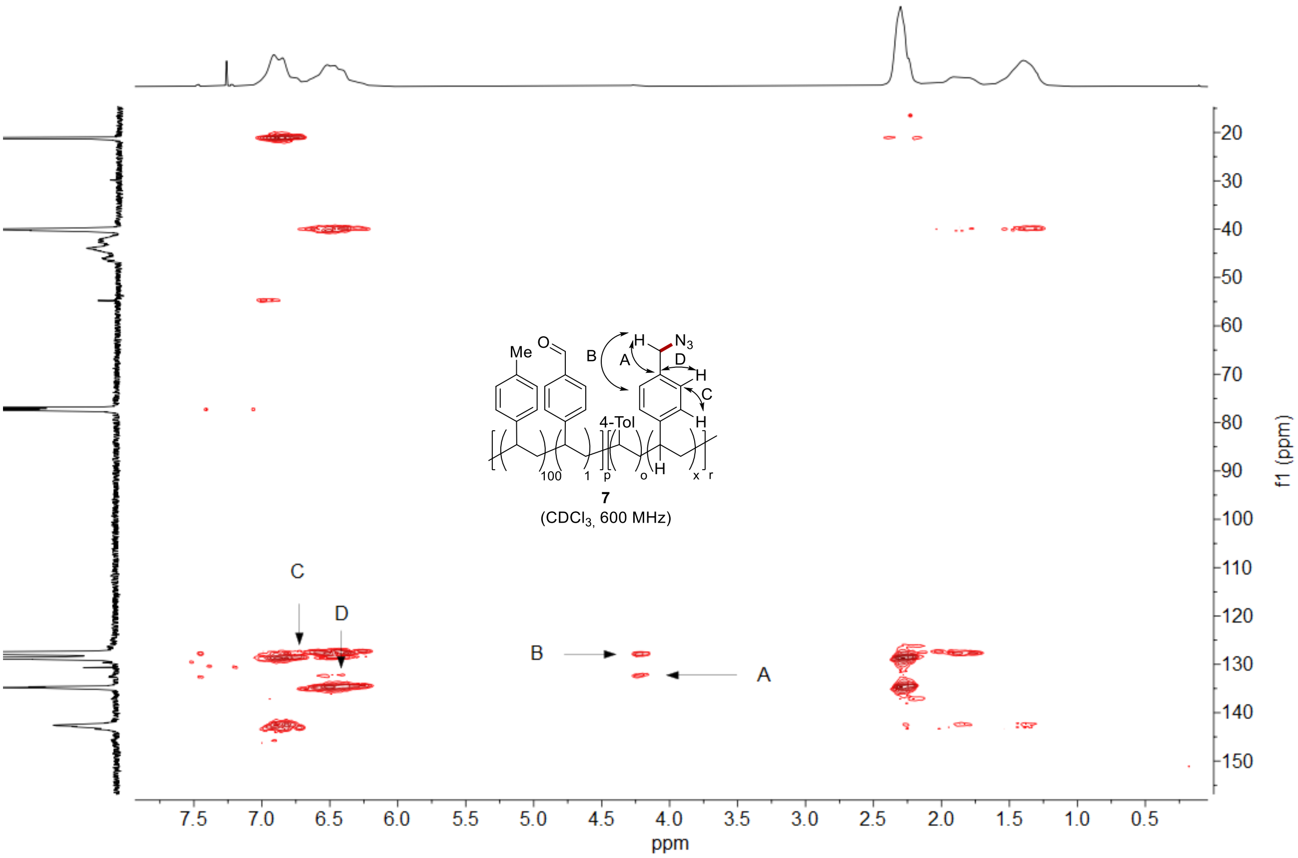


Figure S51. HMBC of **7** in $CDCl_3$. Asterisk marks 1,2-DCB impurities.

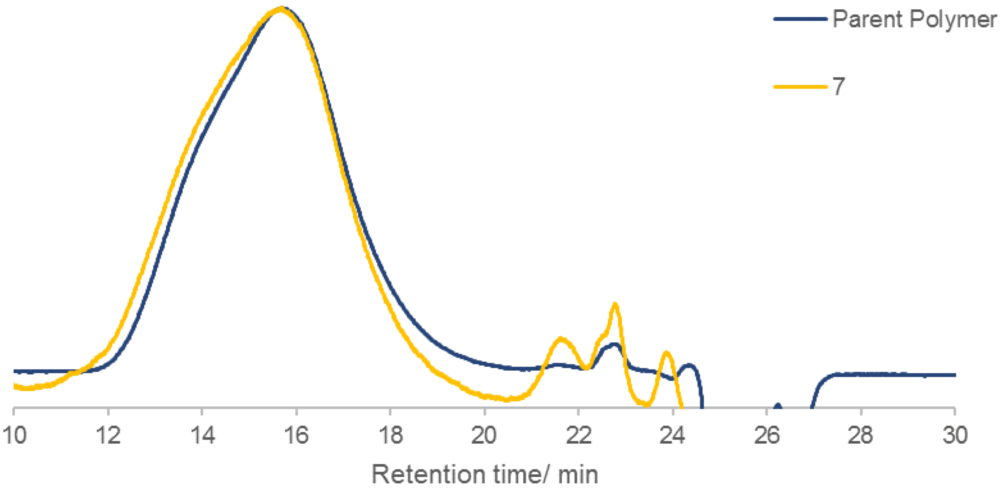


Figure S52. Normalized chromatogram of parent (blue) and modified polymer **7** (yellow).

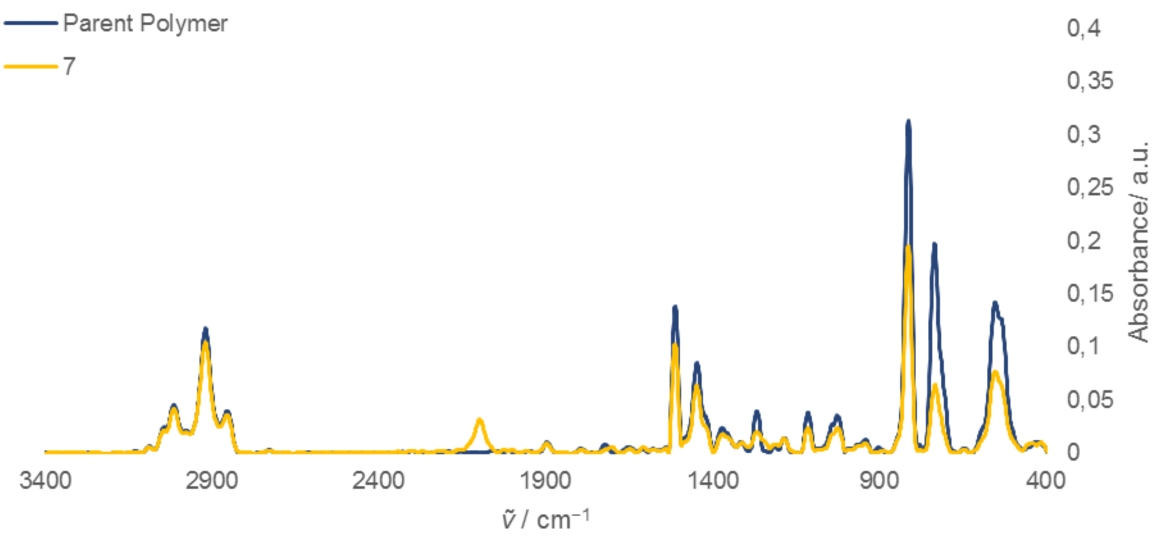


Figure S53. IR spectrum of parent (blue) and modified polymer **7** (yellow) in arbitrary units (a.u.).

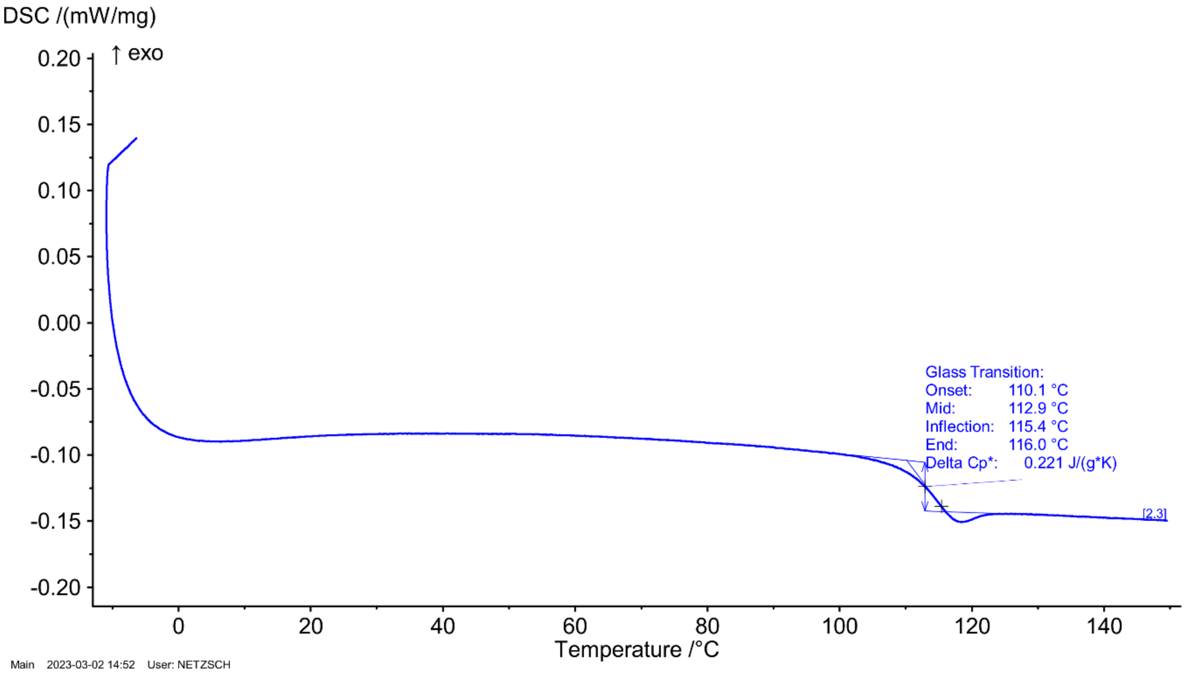


Figure S54. DSC of **7**.

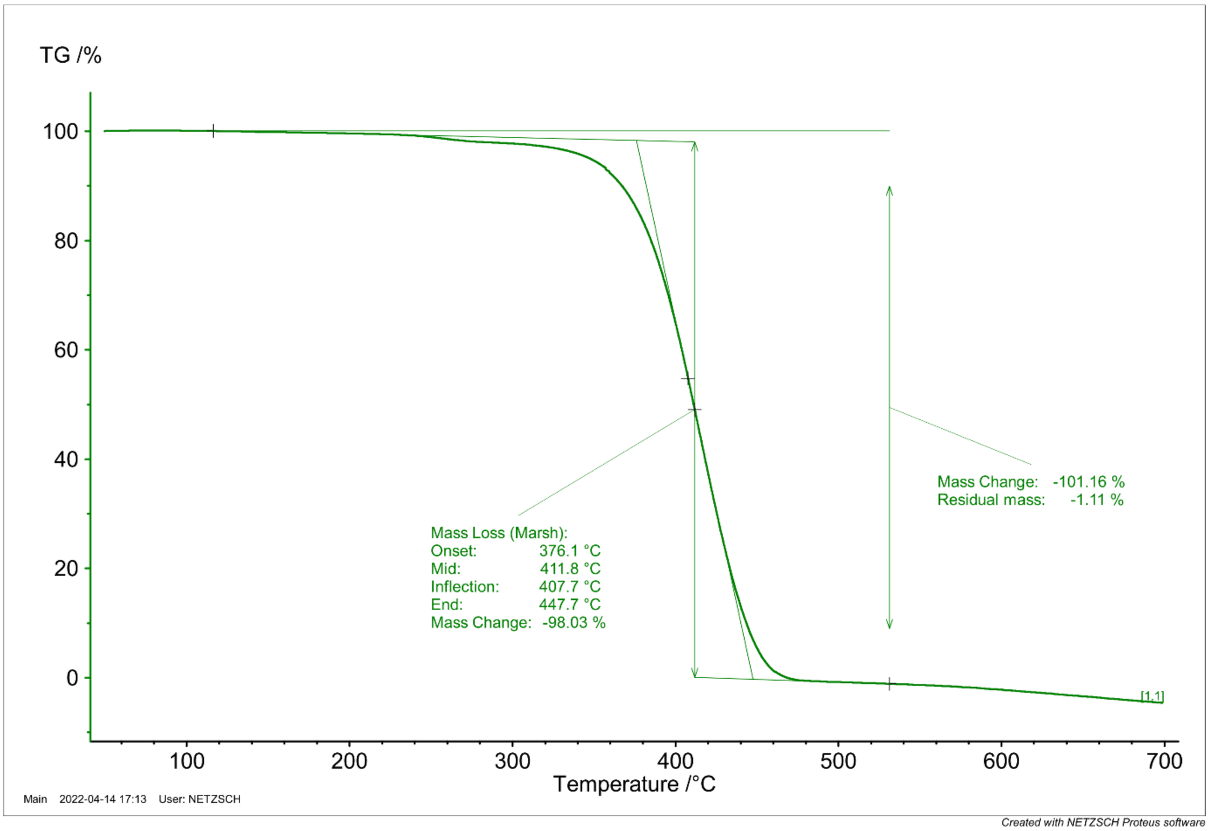


Figure S55. TGA of **7**.

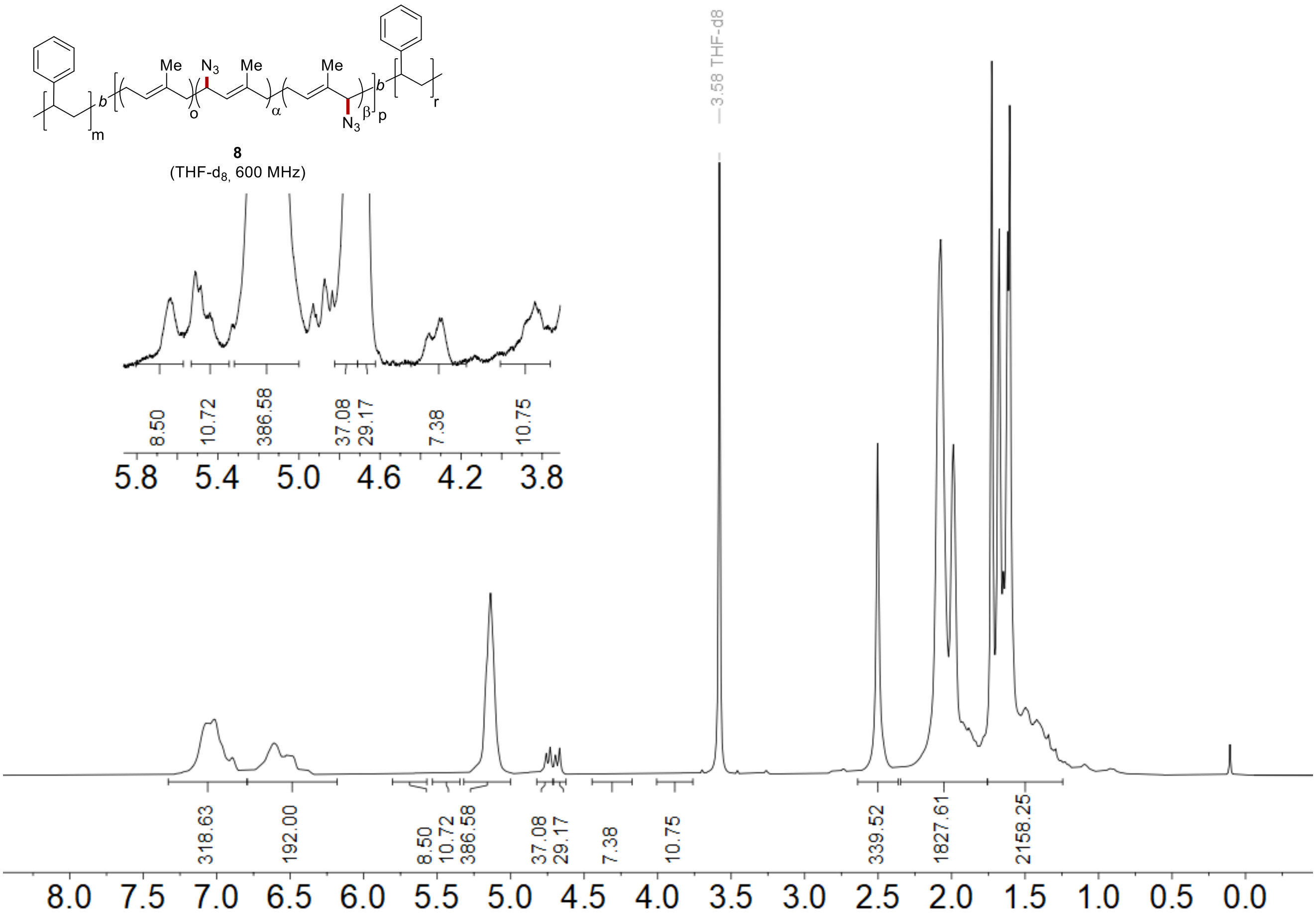


Figure S56. ^{1}H NMR of **8** in THF-d_8.

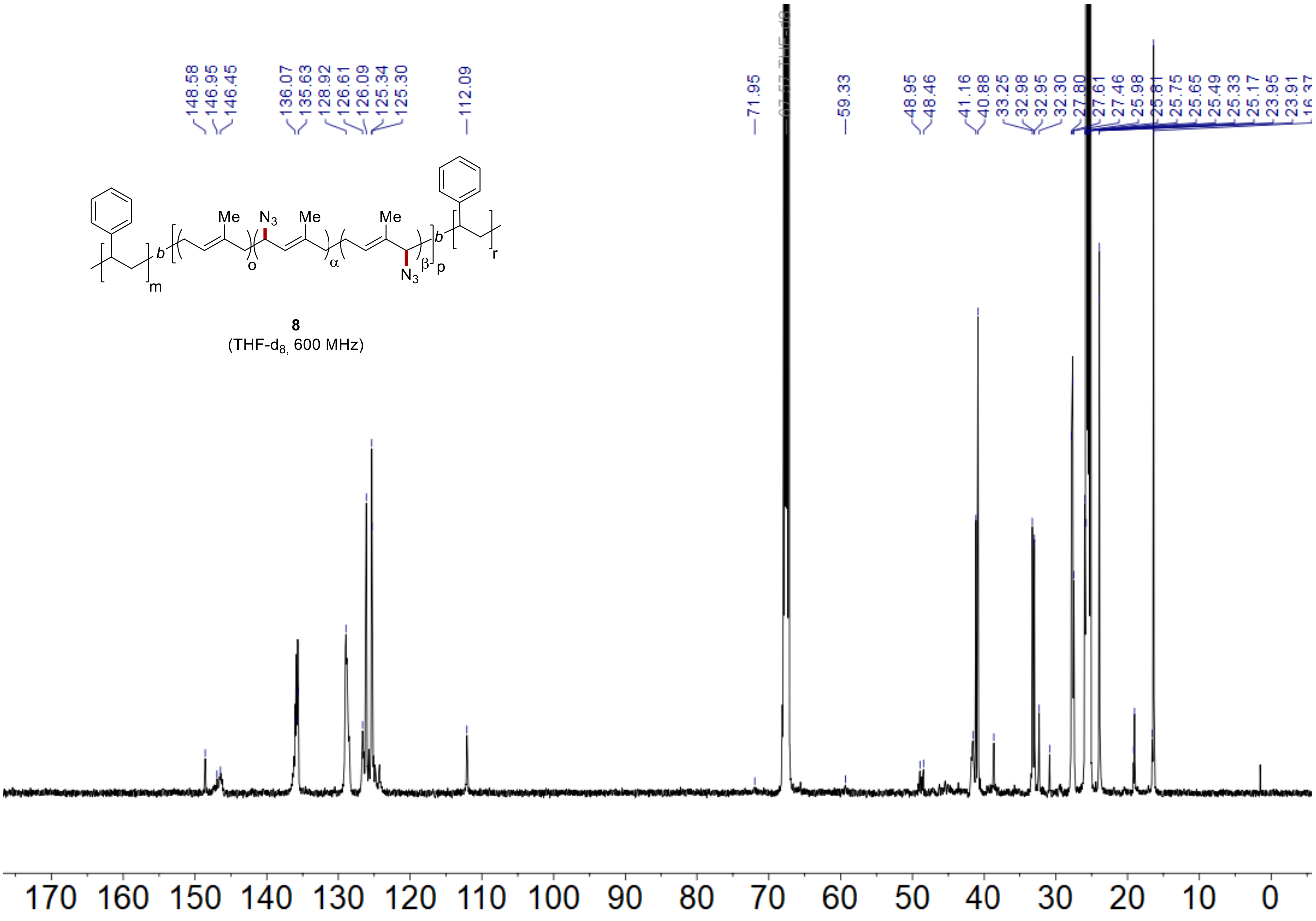


Figure S57. ^{13}C NMR of **8** in THF-d_8.

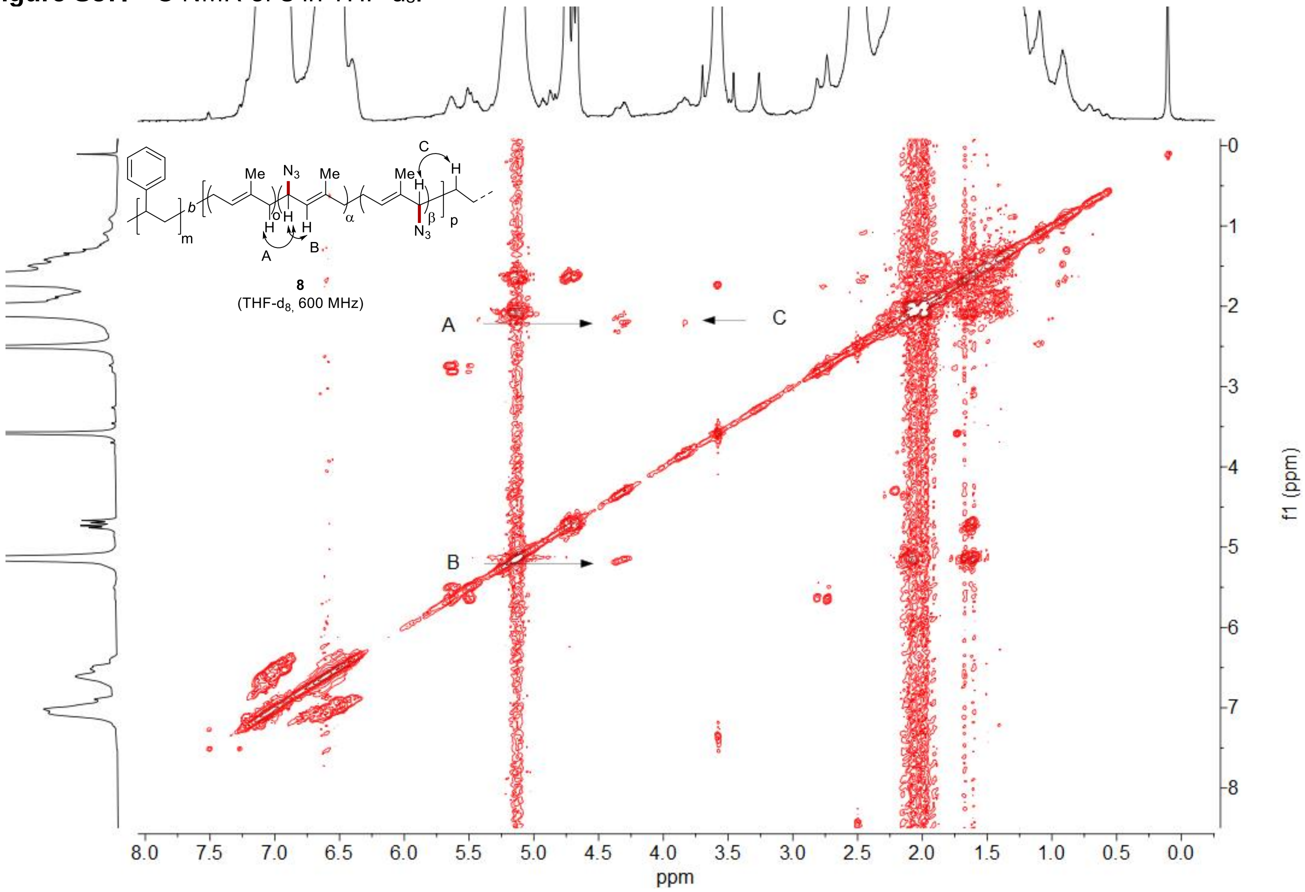


Figure S58. COSY of **8** in THF-d_8.

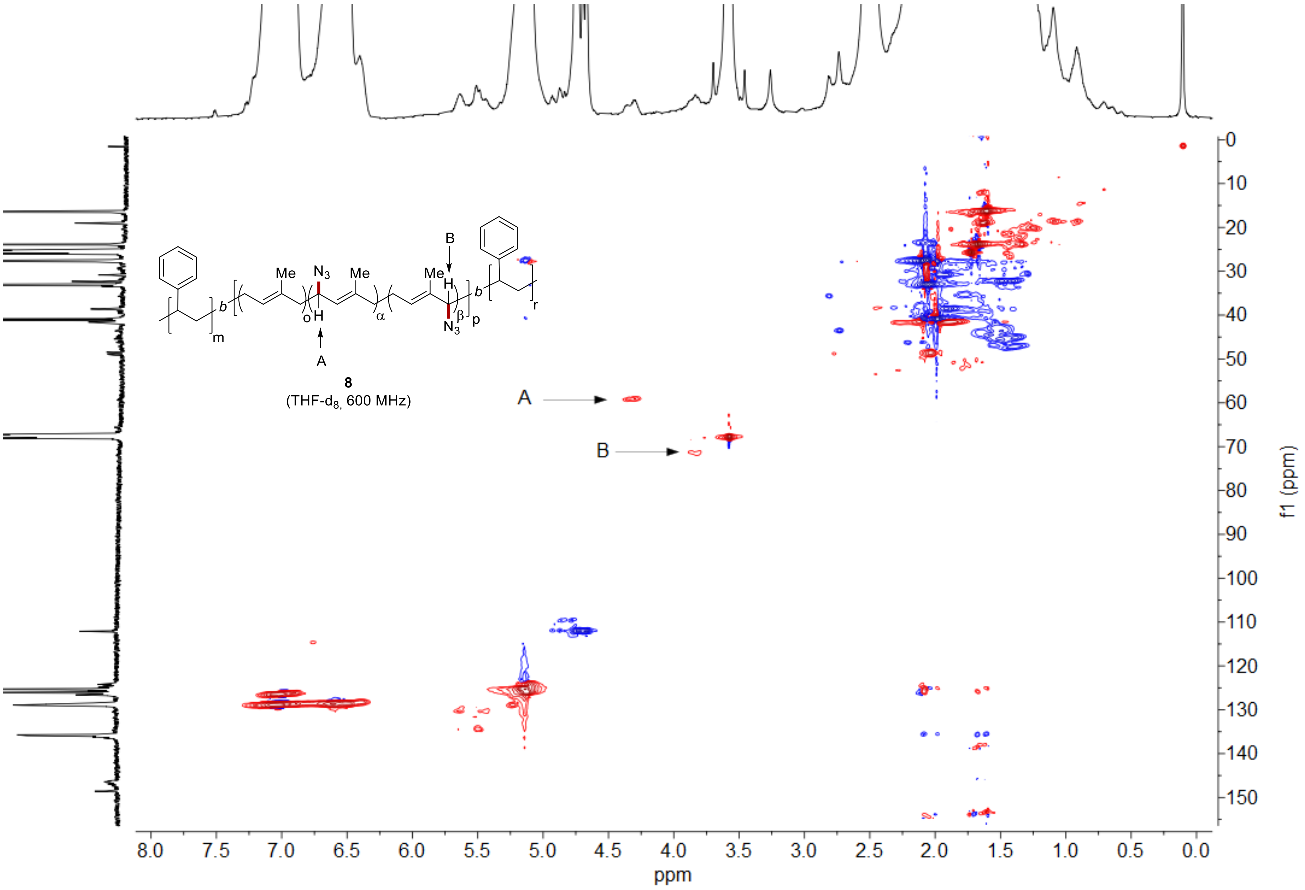


Figure S59. HSQC of **8** in THF-d_8.

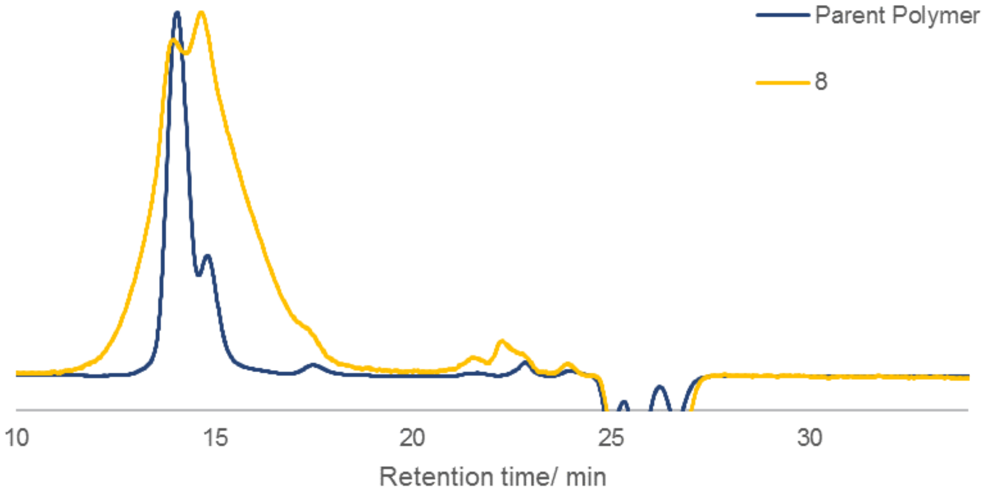


Figure S60. Normalized chromatogram of parent (blue) and modified polymer **8** (yellow).

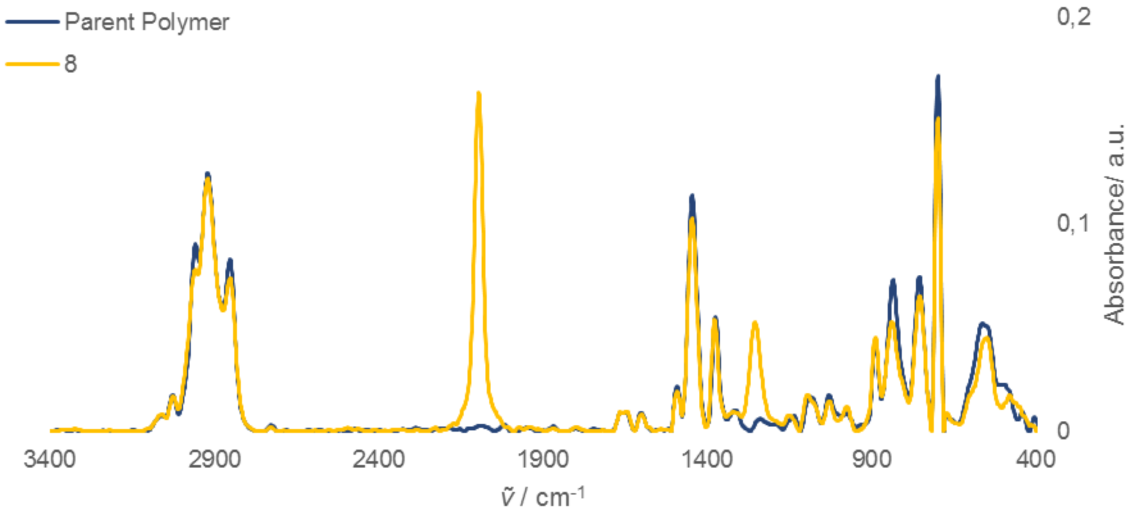


Figure S61. IR spectrum of parent (blue) and modified polymer **8** (yellow) in arbitrary units (a.u.).

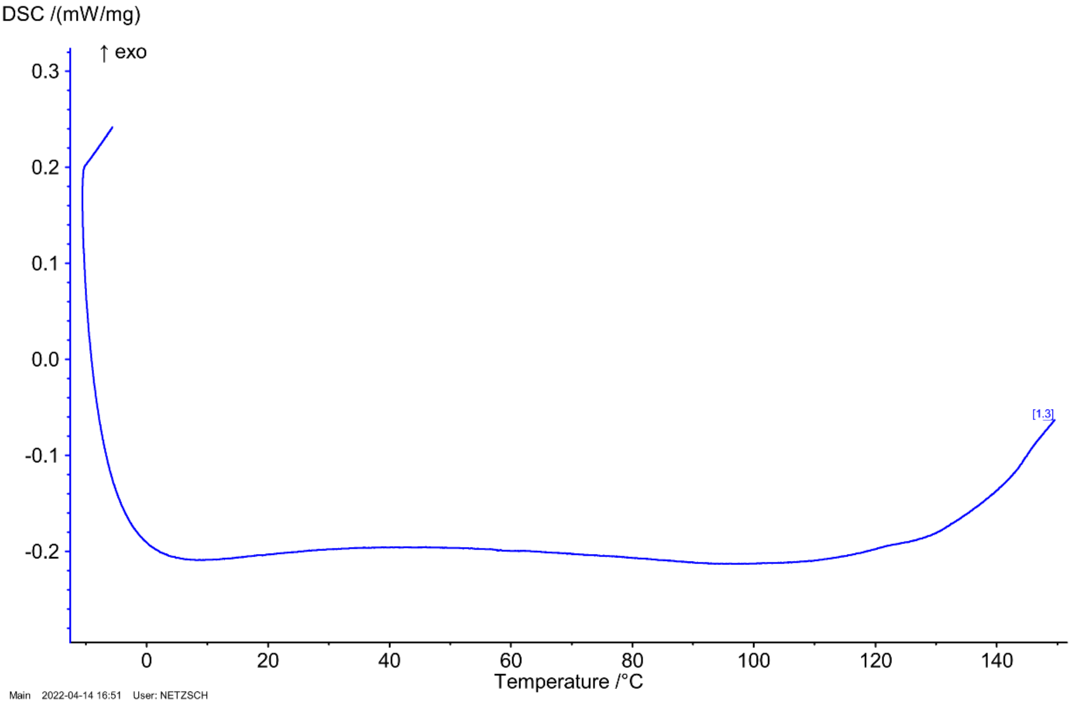


Figure S62. DSC of **8**.

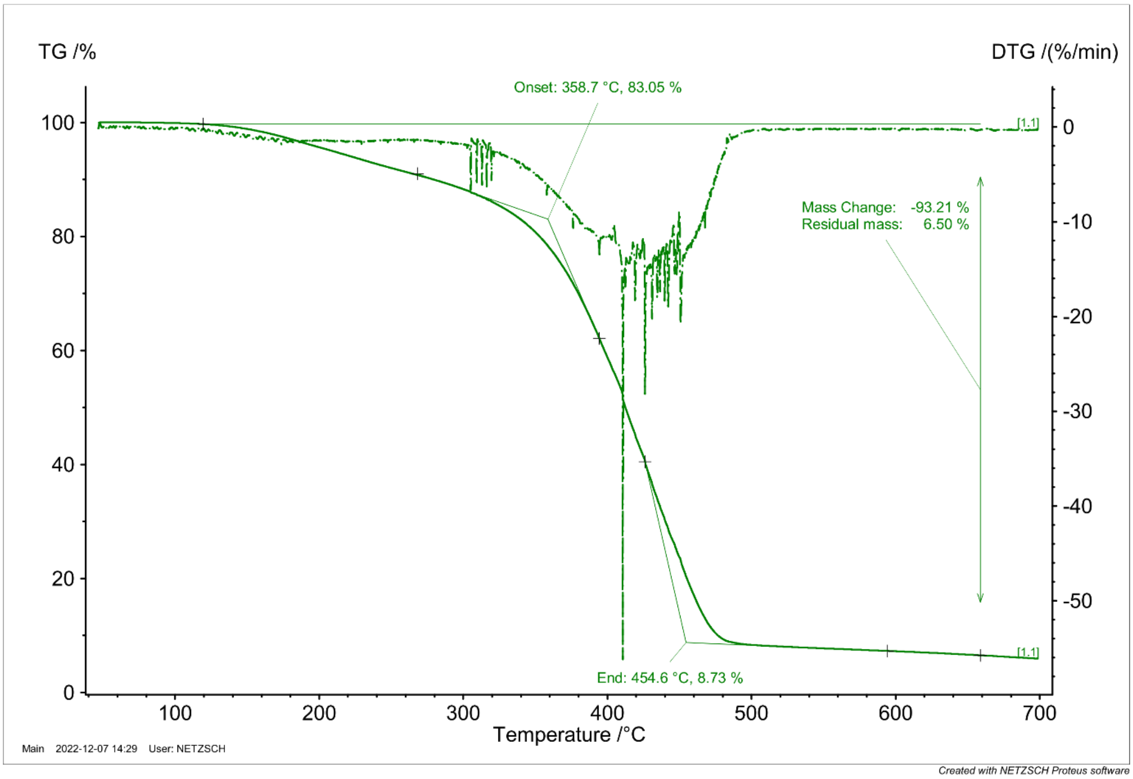


Figure S63. TGA of **8**.

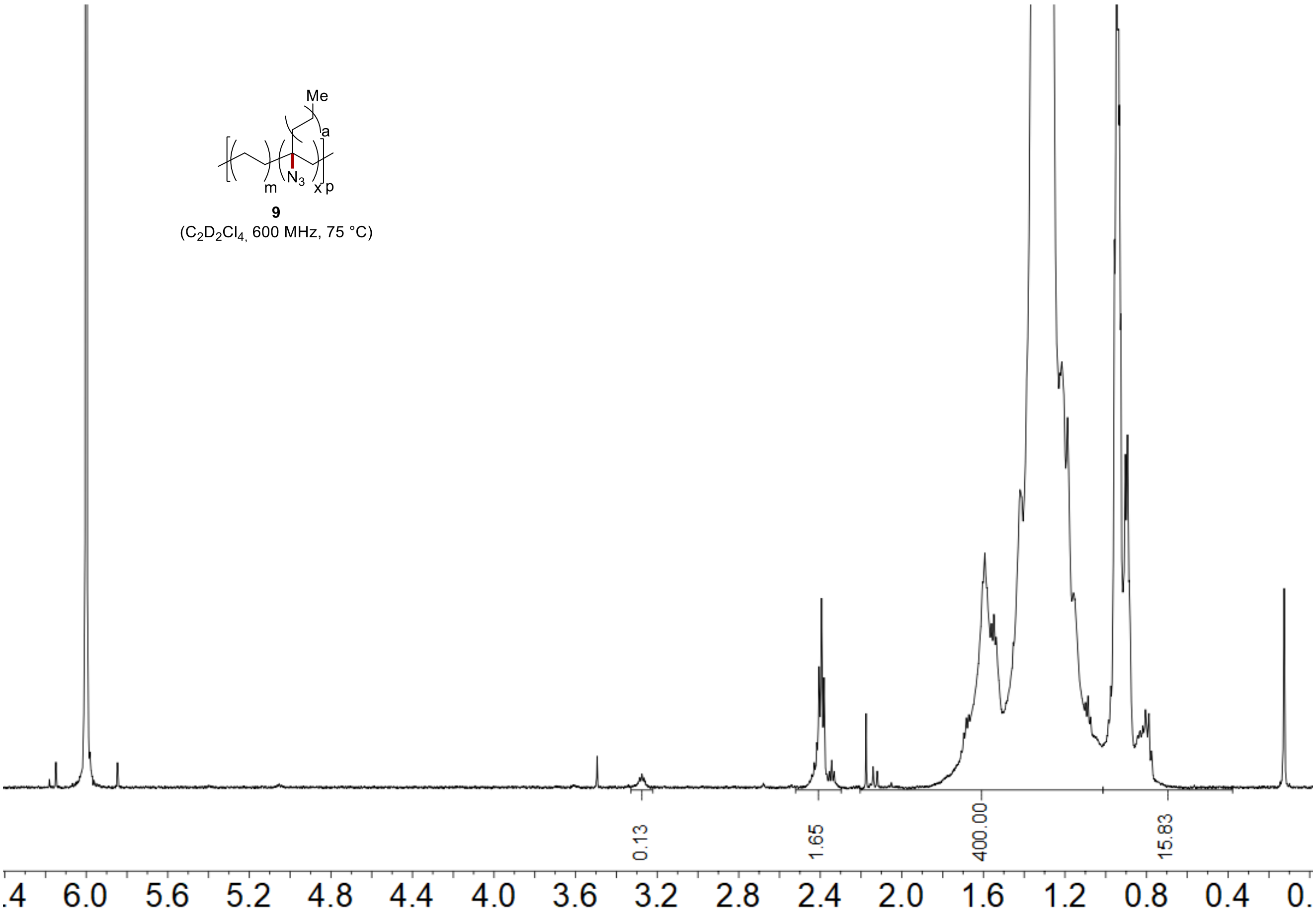


Figure S64. ^{1}H NMR of **9** in $C_2D_2Cl_4$ at 75 °C.

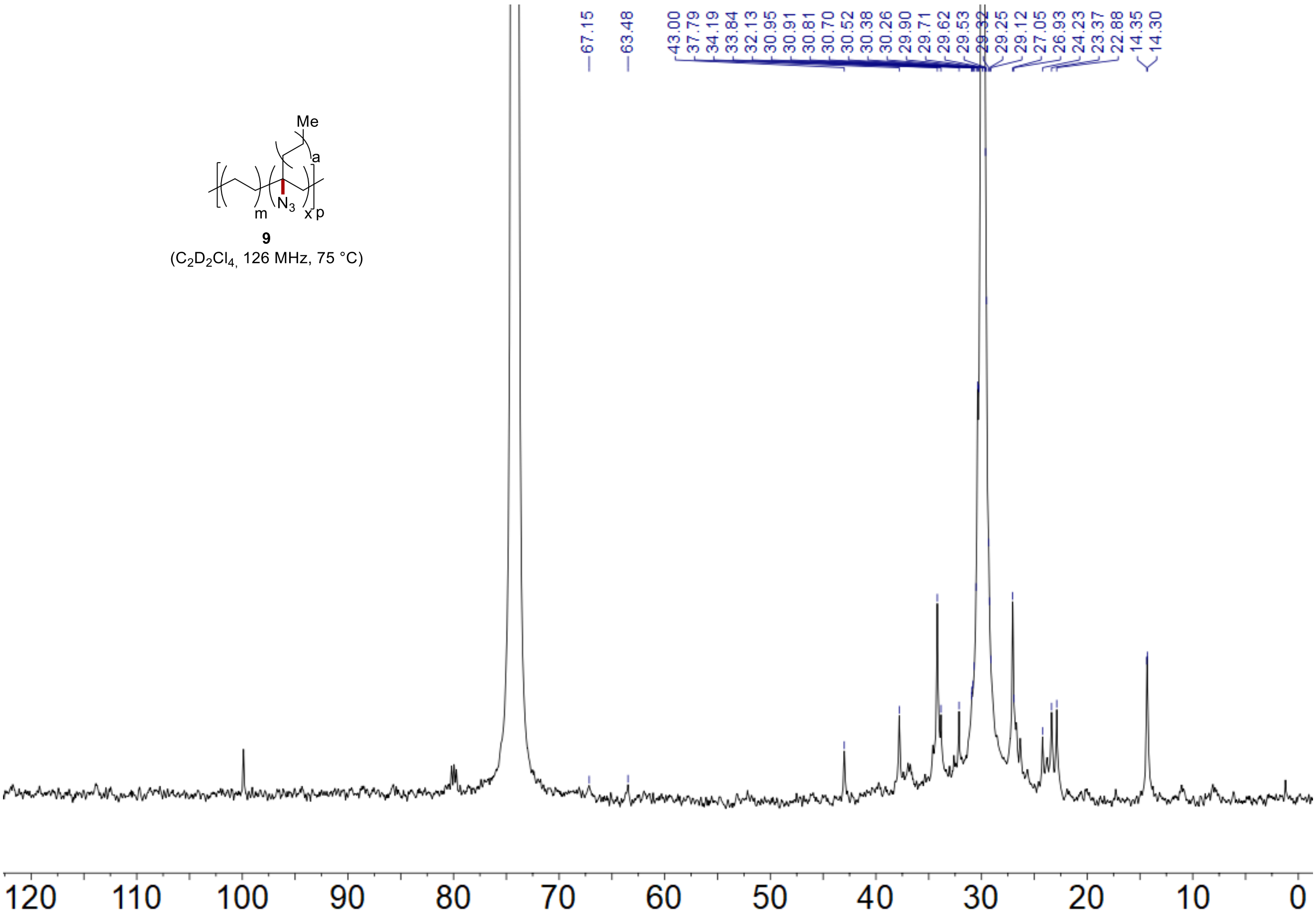


Figure S65. ^{13}C NMR of **9** in $C_2D_2Cl_4$ at 75 °C.

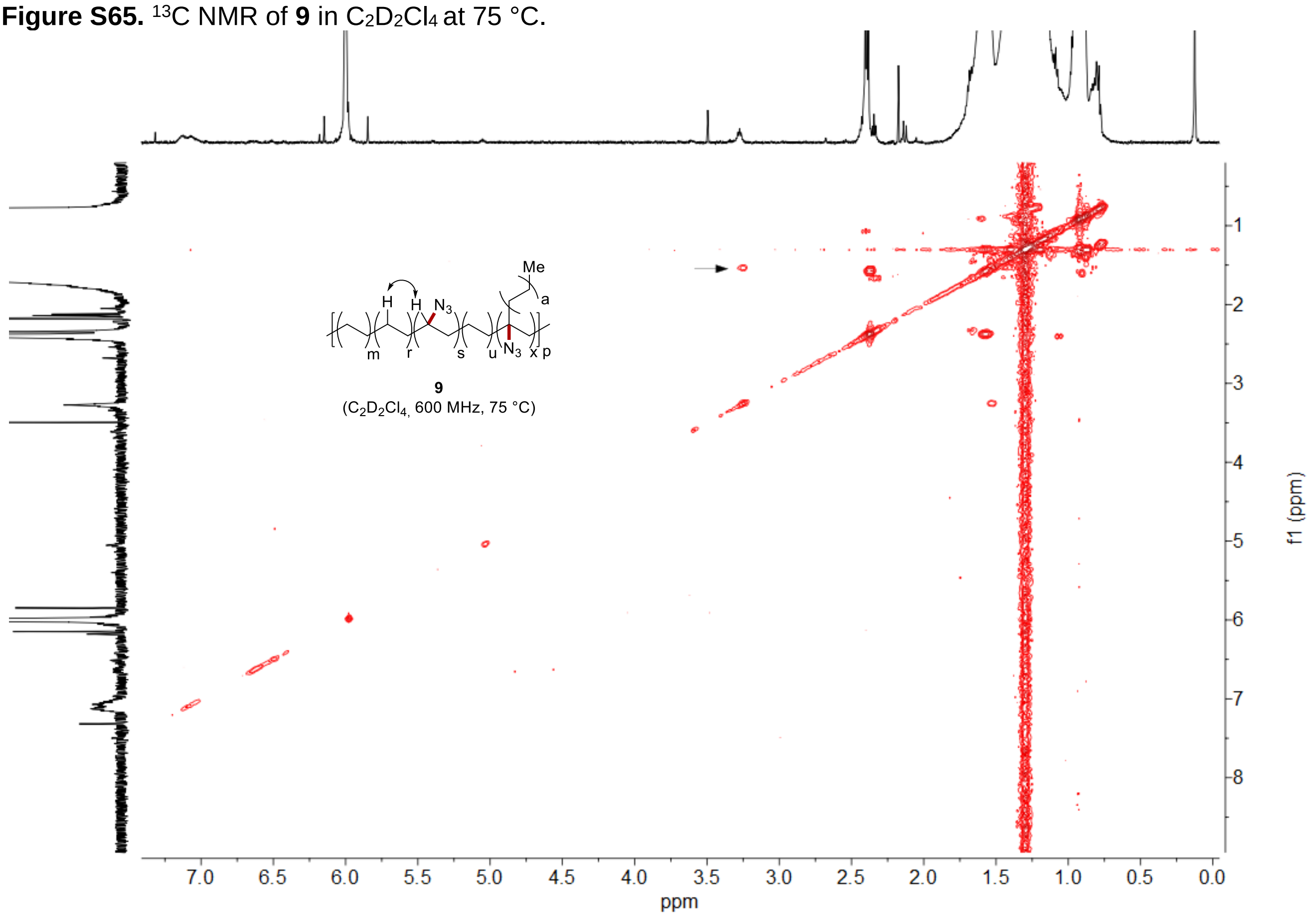


Figure S66. COSY of **9** in $C_2D_2Cl_4$ at 75 °C.

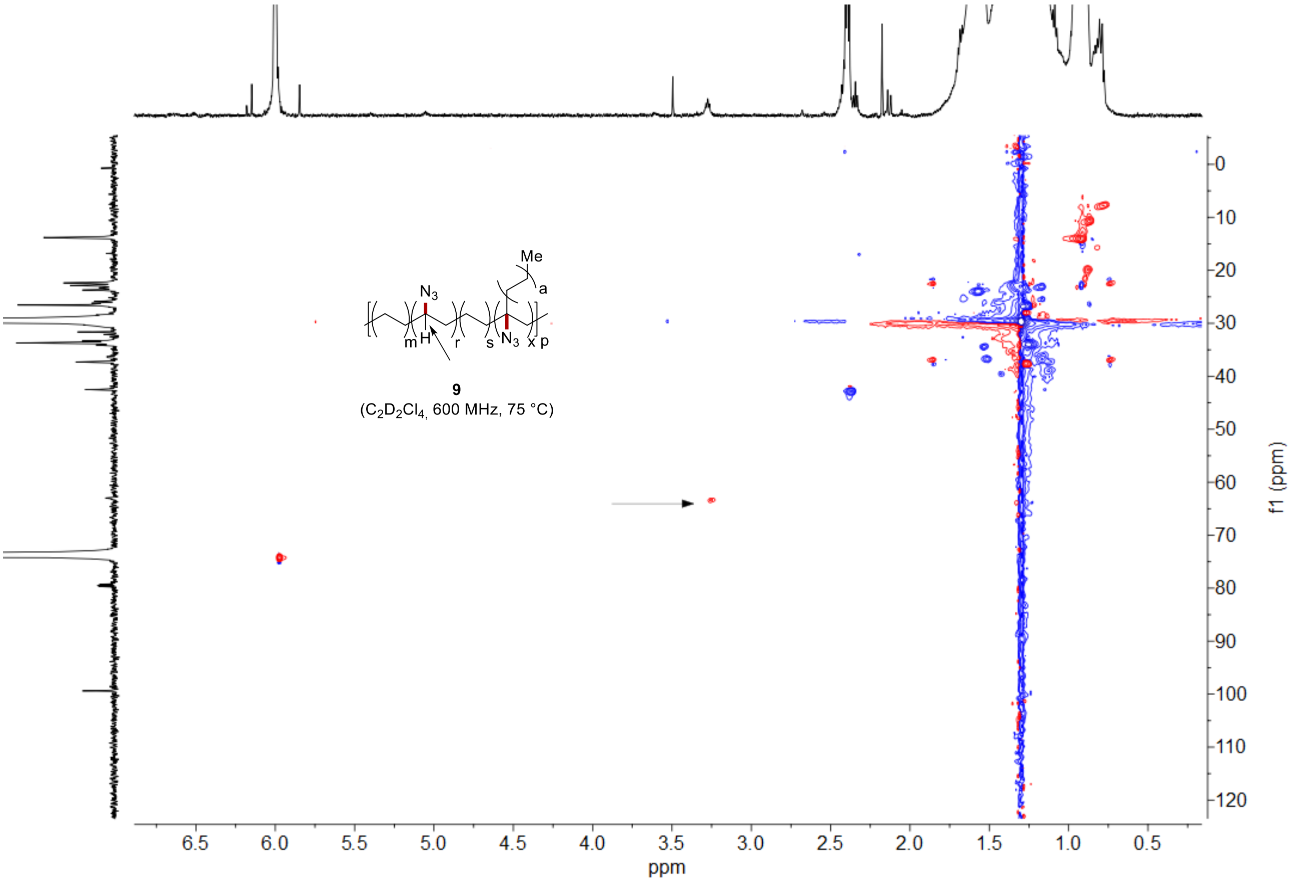


Figure S67. HSQC of **9** in $C_2D_2Cl_4$ at 75 °C.

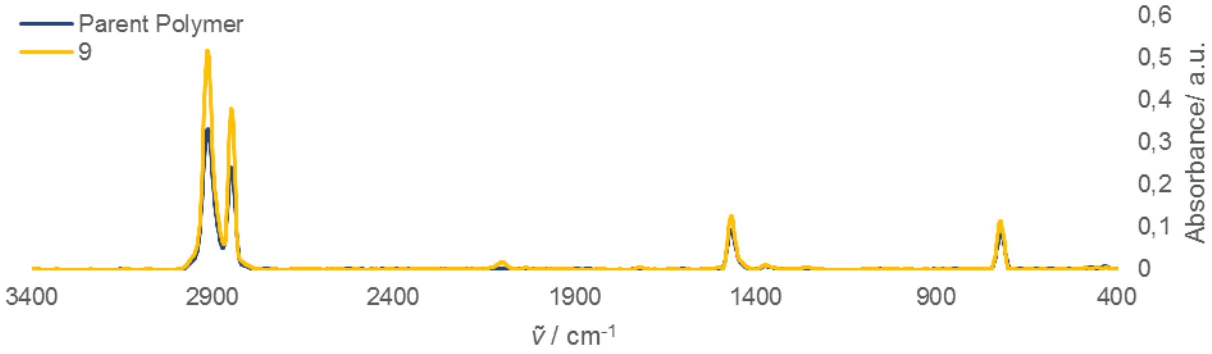


Figure S68. IR spectrum of parent (blue) and modified polymer **9** (yellow) in arbitrary units (a.u.).

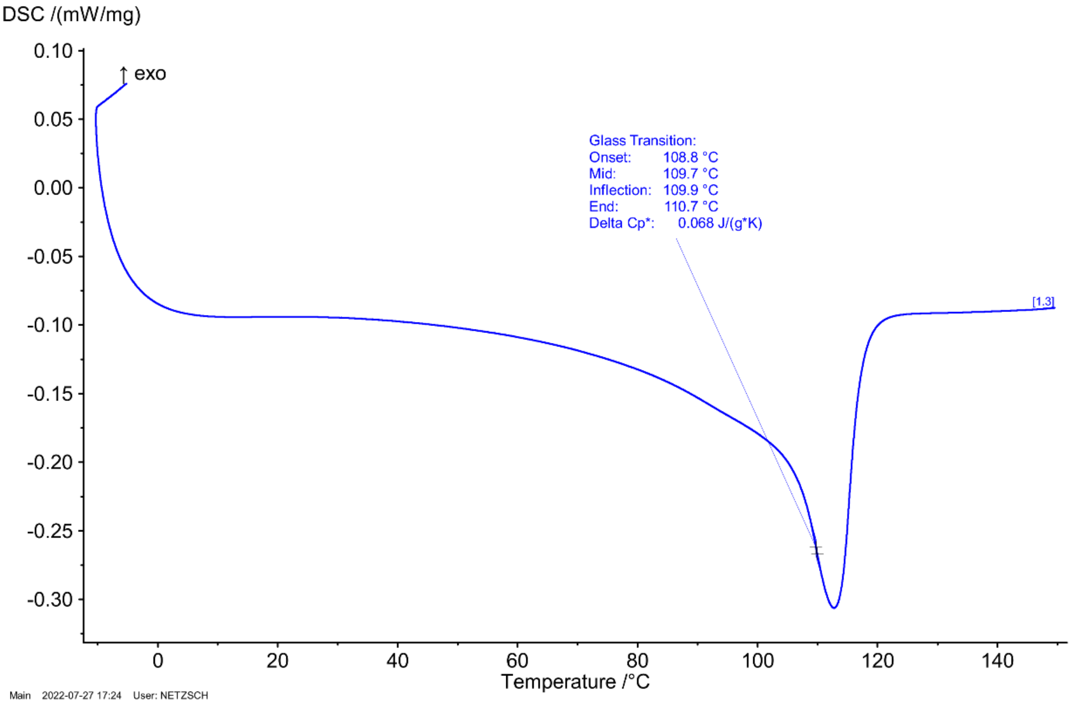


Figure S69. DSC of **9**.

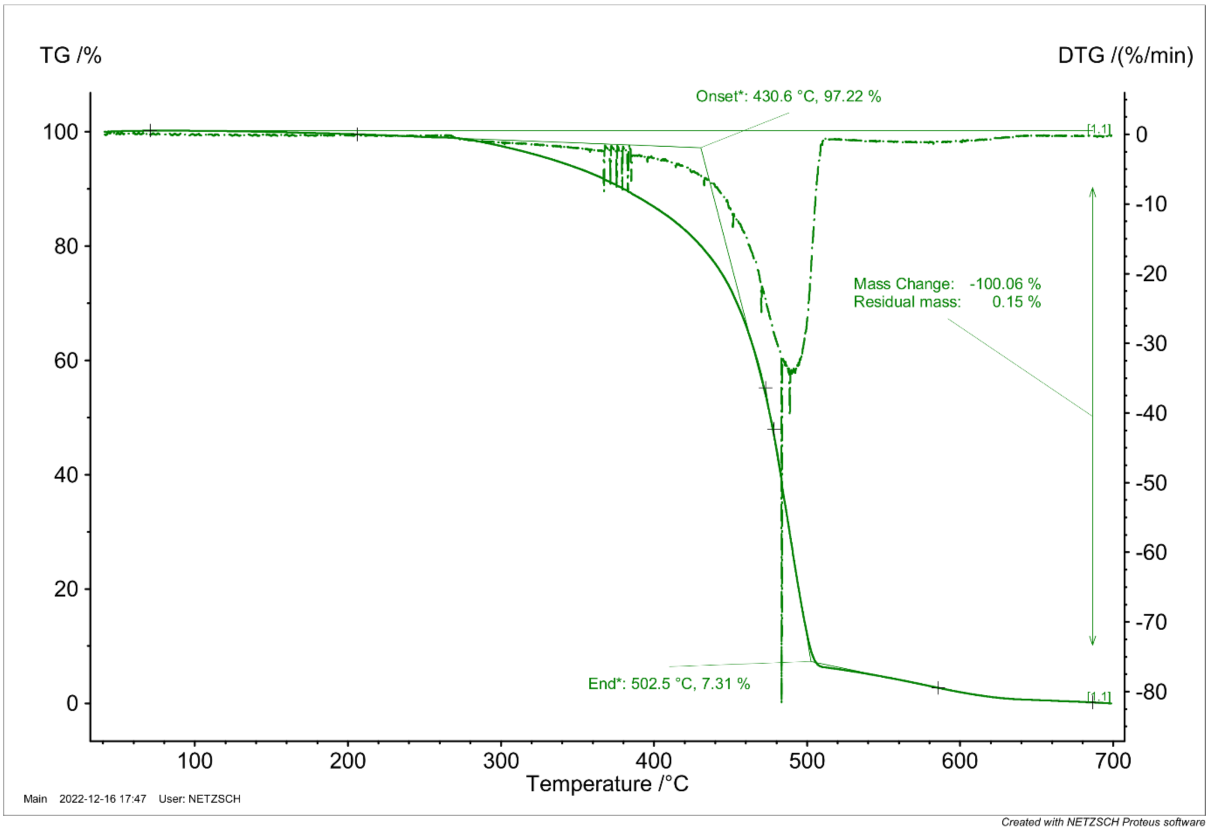


Figure S70. TGA of **9**.

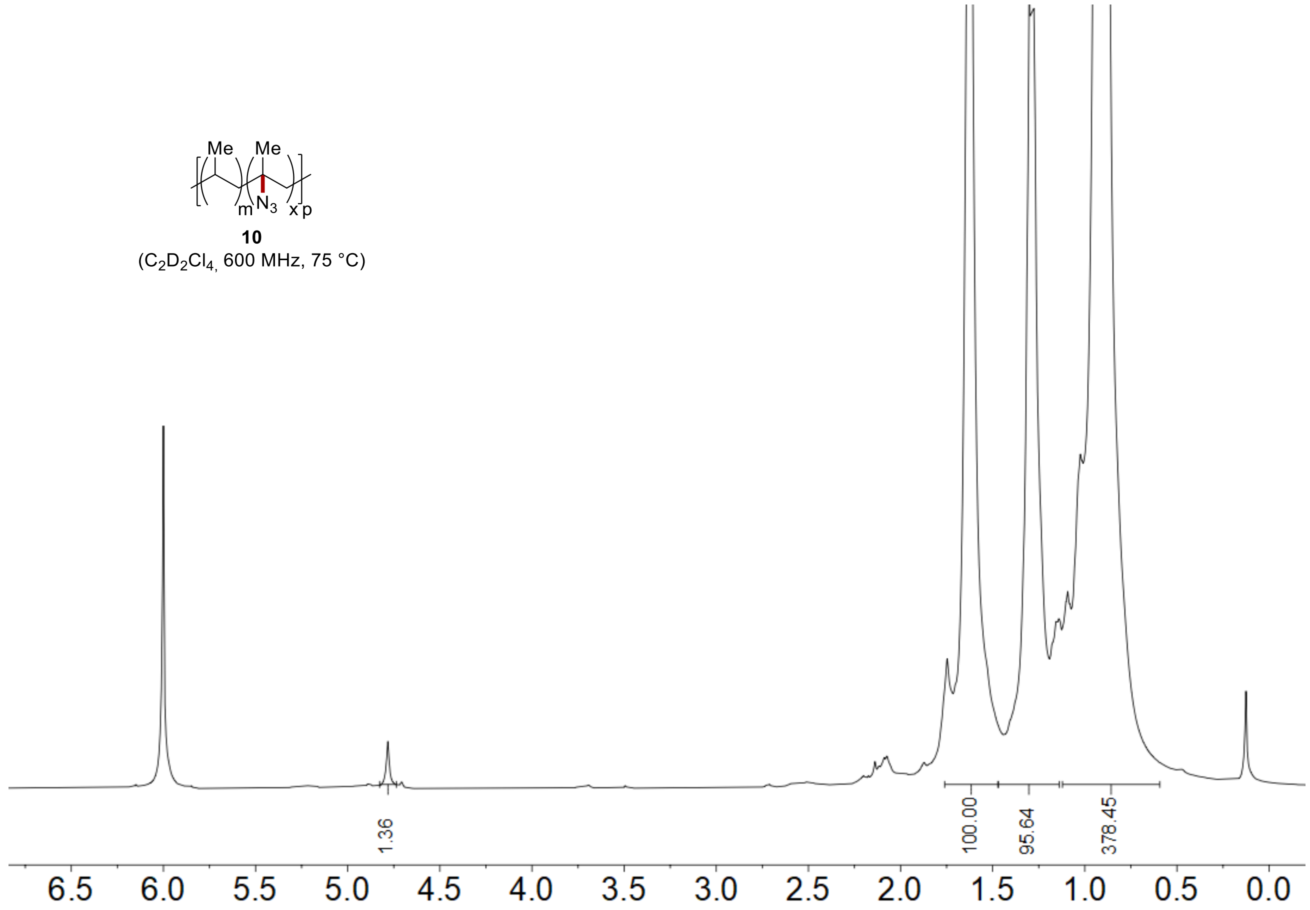


Figure S71. ^{1}H NMR of **10** in $C_2D_2Cl_4$ at 75 °C.

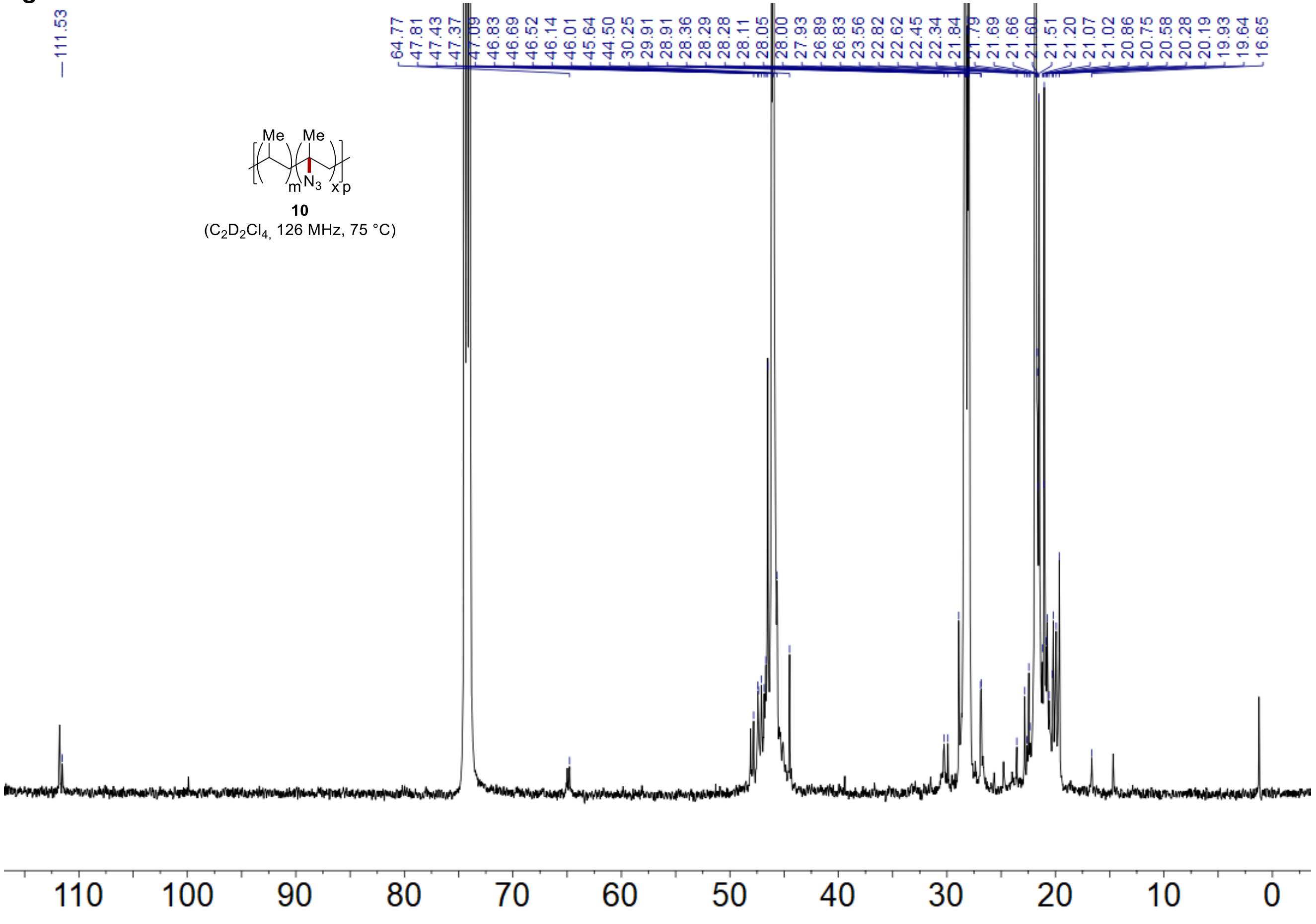


Figure S72. ^{13}C NMR of **10** in $C_2D_2Cl_4$ at 75 °C.

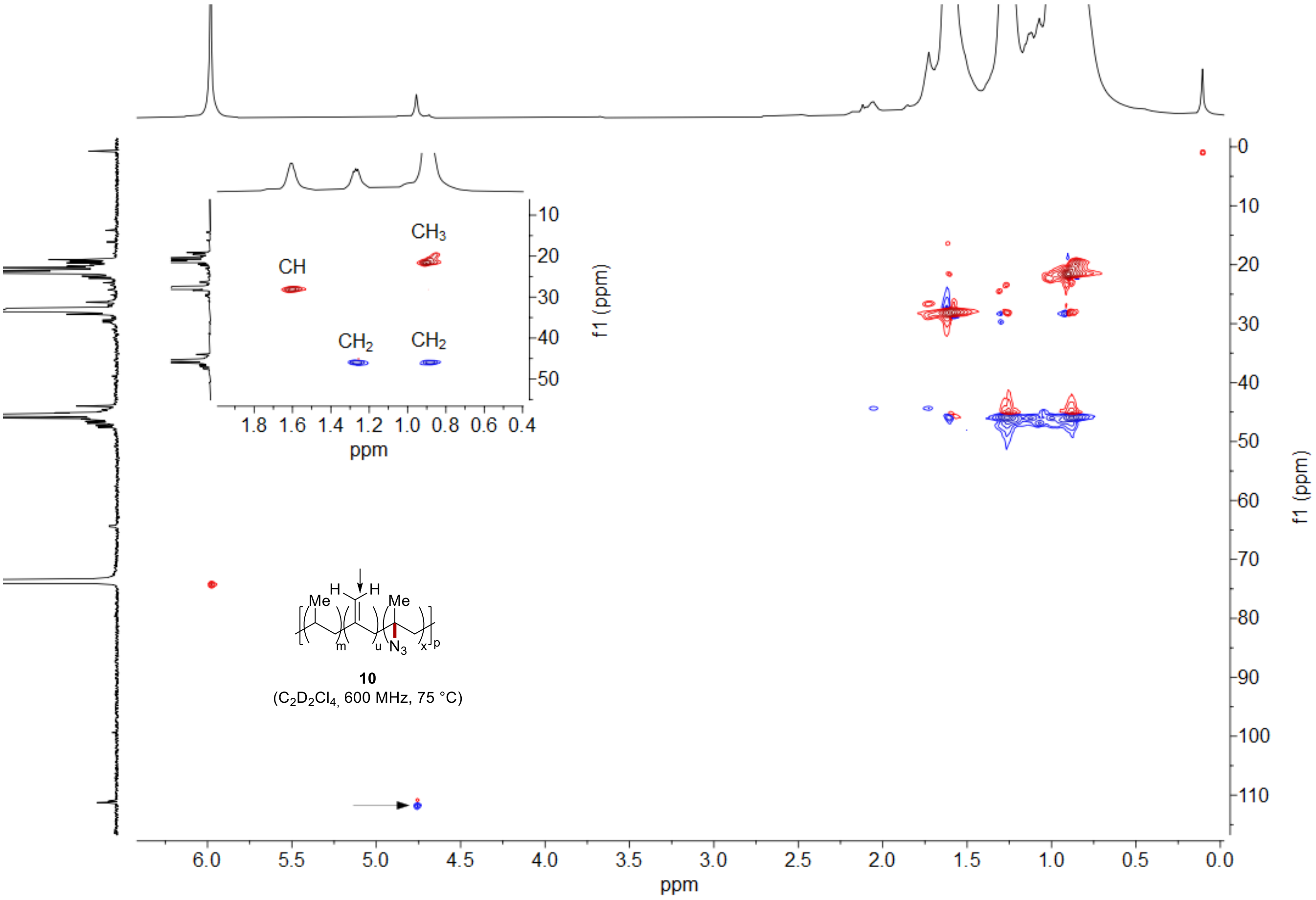


Figure S73. HSQC of **10** in $C_2D_2Cl_4$ at 75 °C.

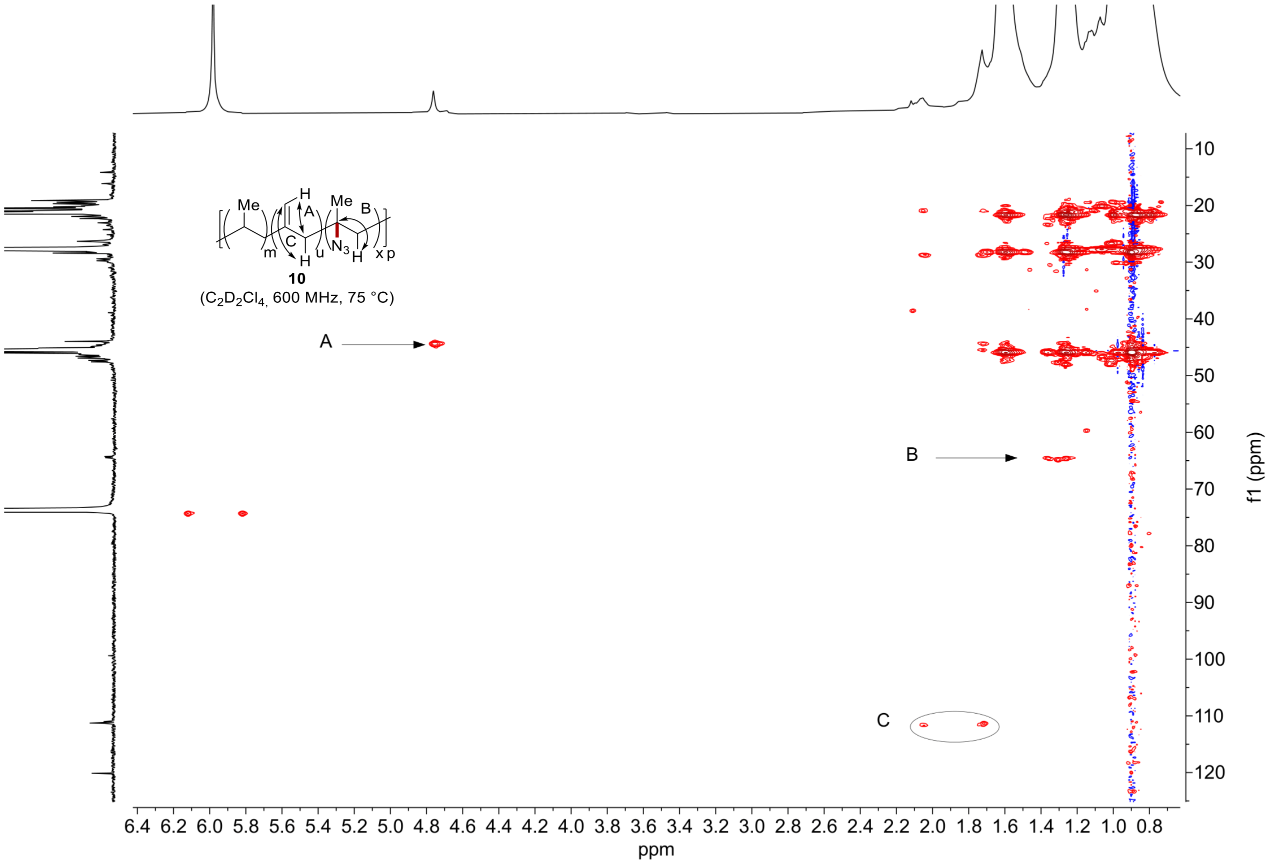


Figure S74. HMBC of **10** in $C_2D_2Cl_4$ at 75 °C.

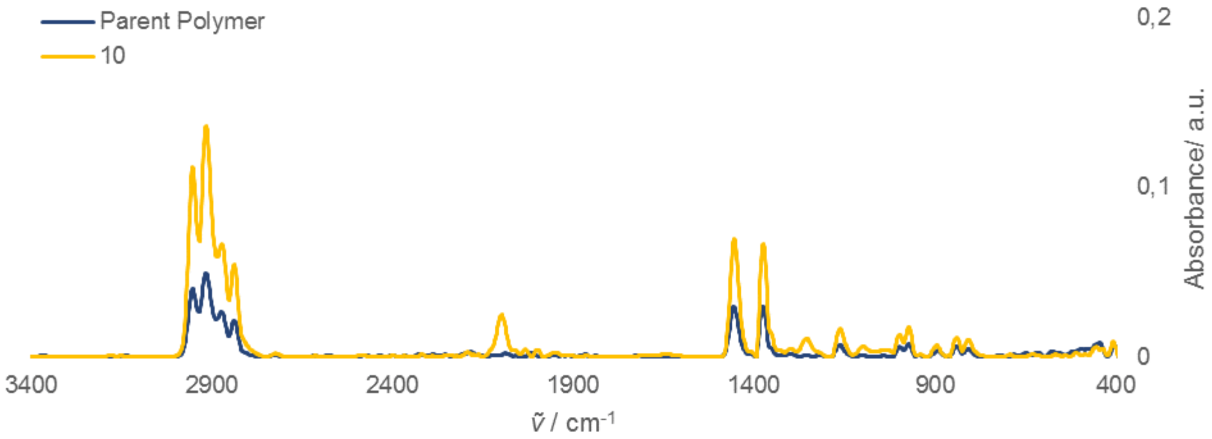


Figure S75. IR spectrum of parent (blue) and modified polymer **10** (yellow) in arbitrary units (a.u.).

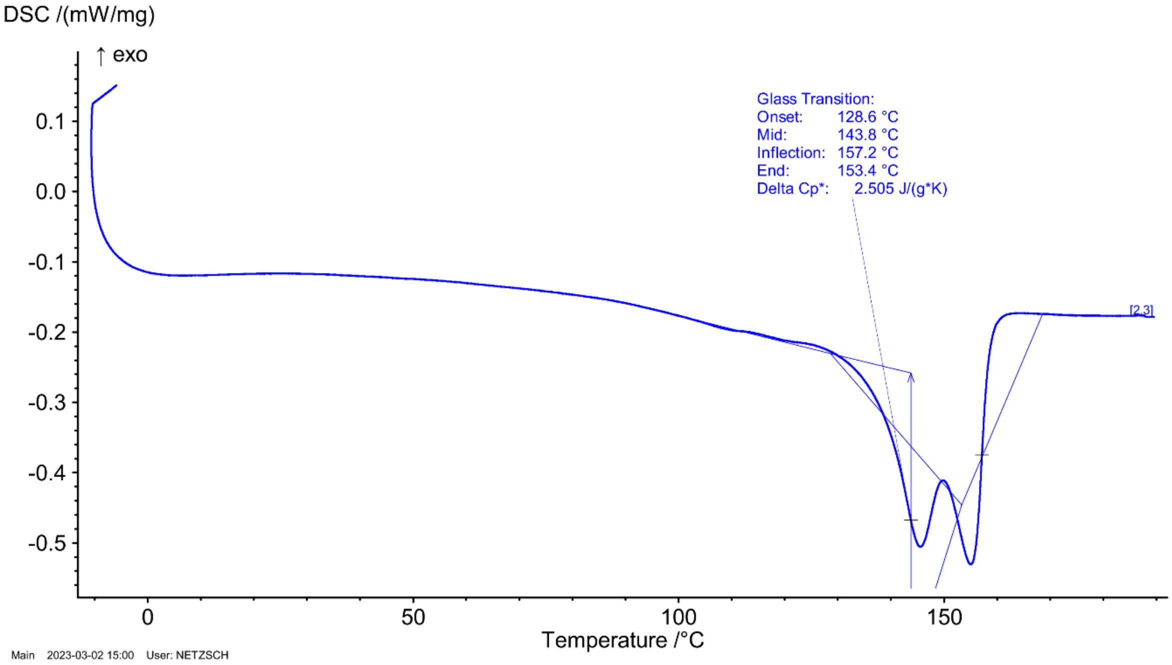


Figure S76. DSC of **10**.

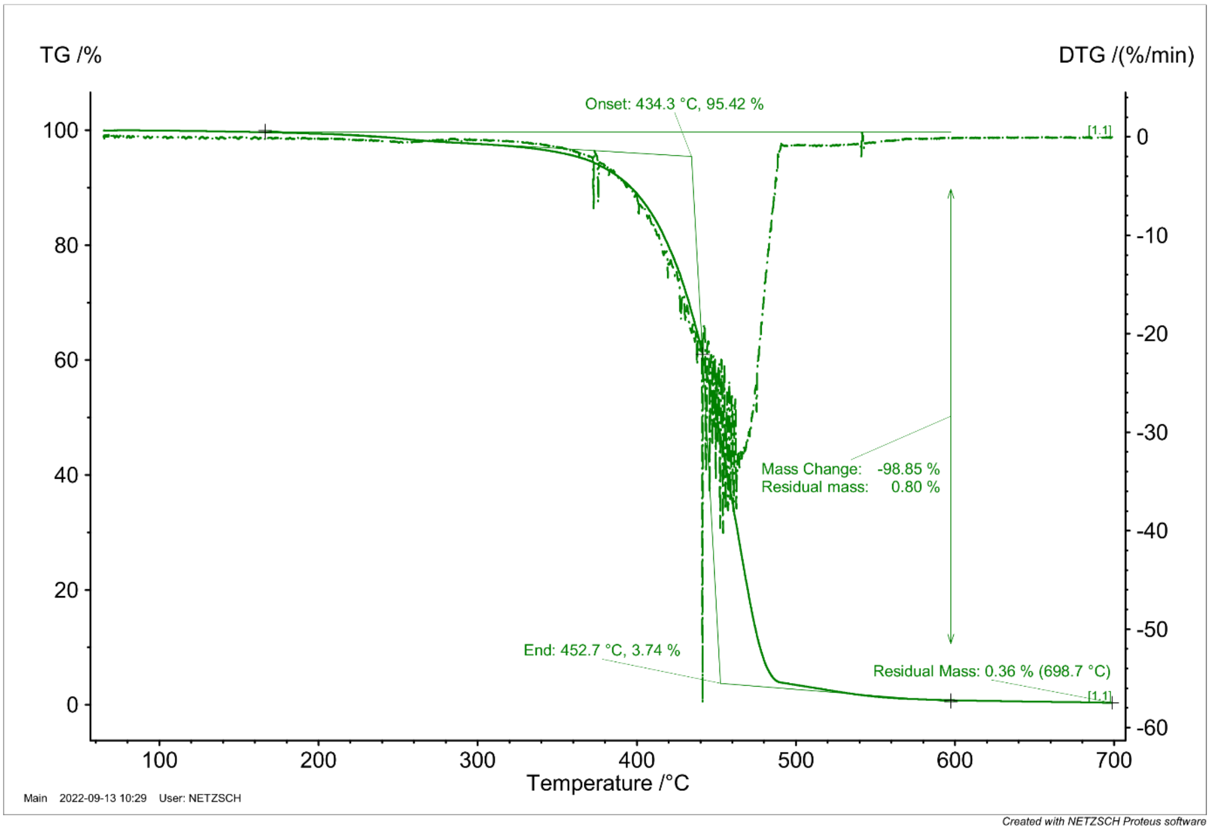


Figure S77. TGA of **10**.

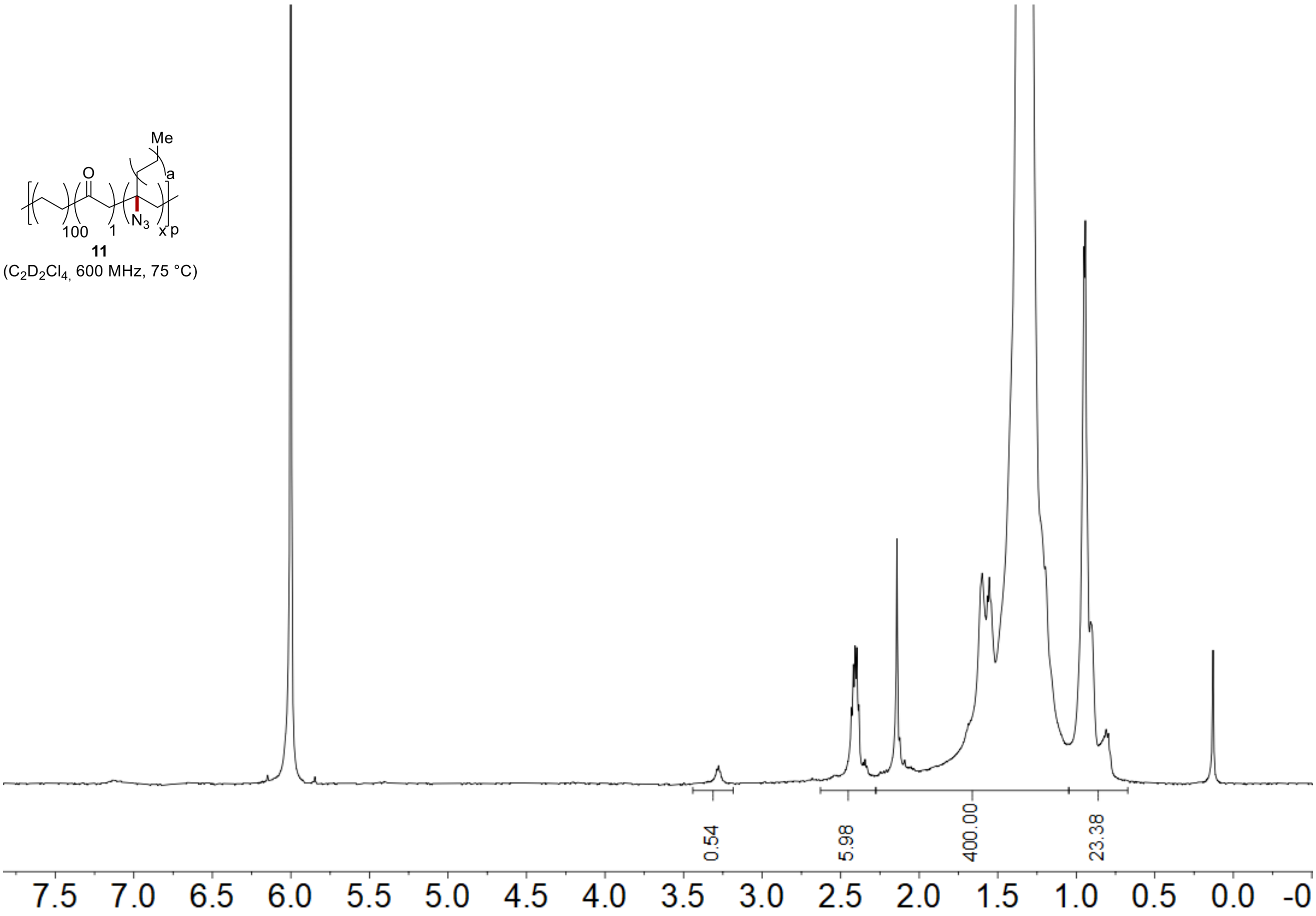


Figure S78. ^{1}H NMR of **11** in $C_2D_2Cl_4$ at 75 °C.

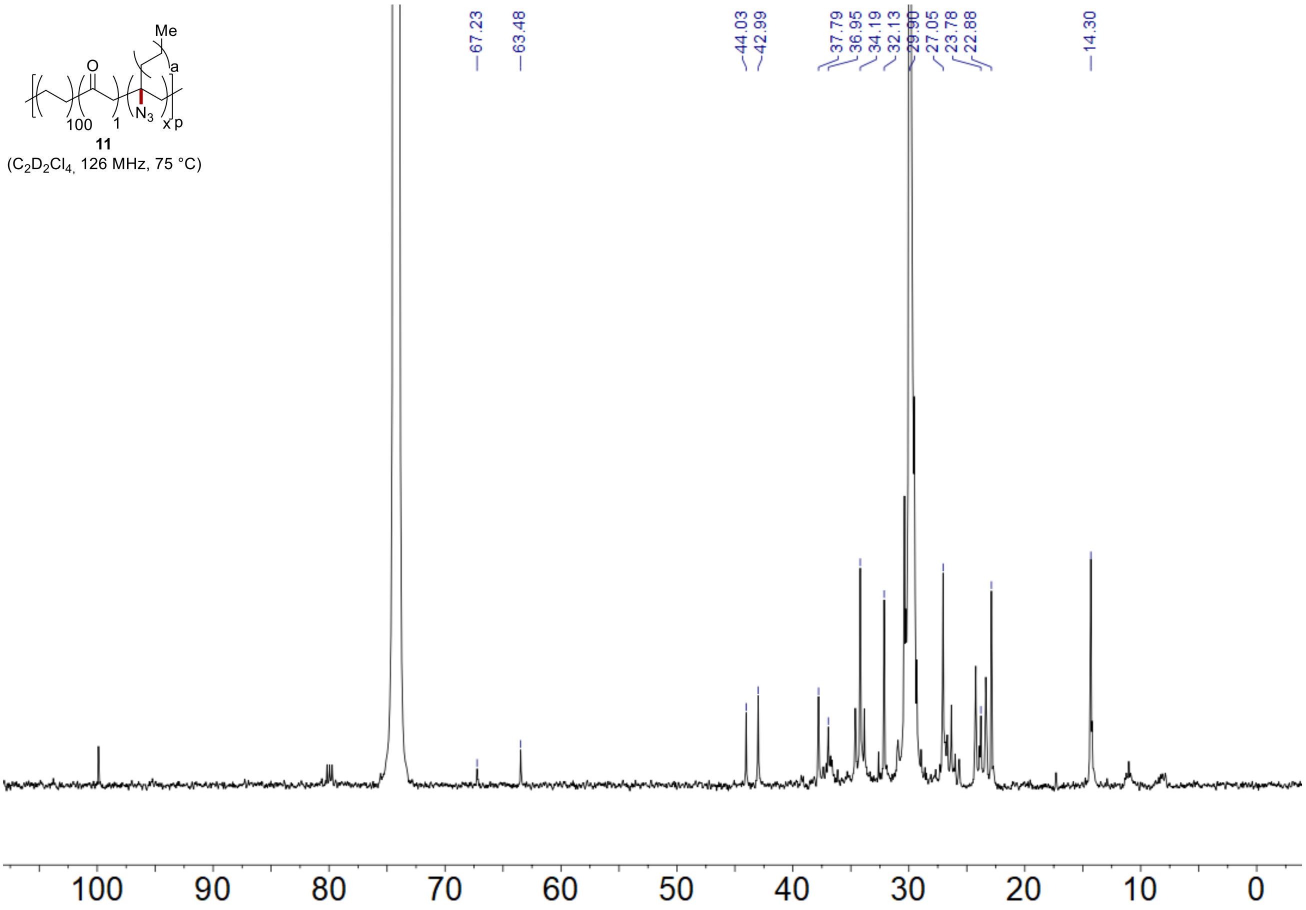


Figure S79. ^{13}C NMR of **11** in $C_2D_2Cl_4$ at 75 °C.

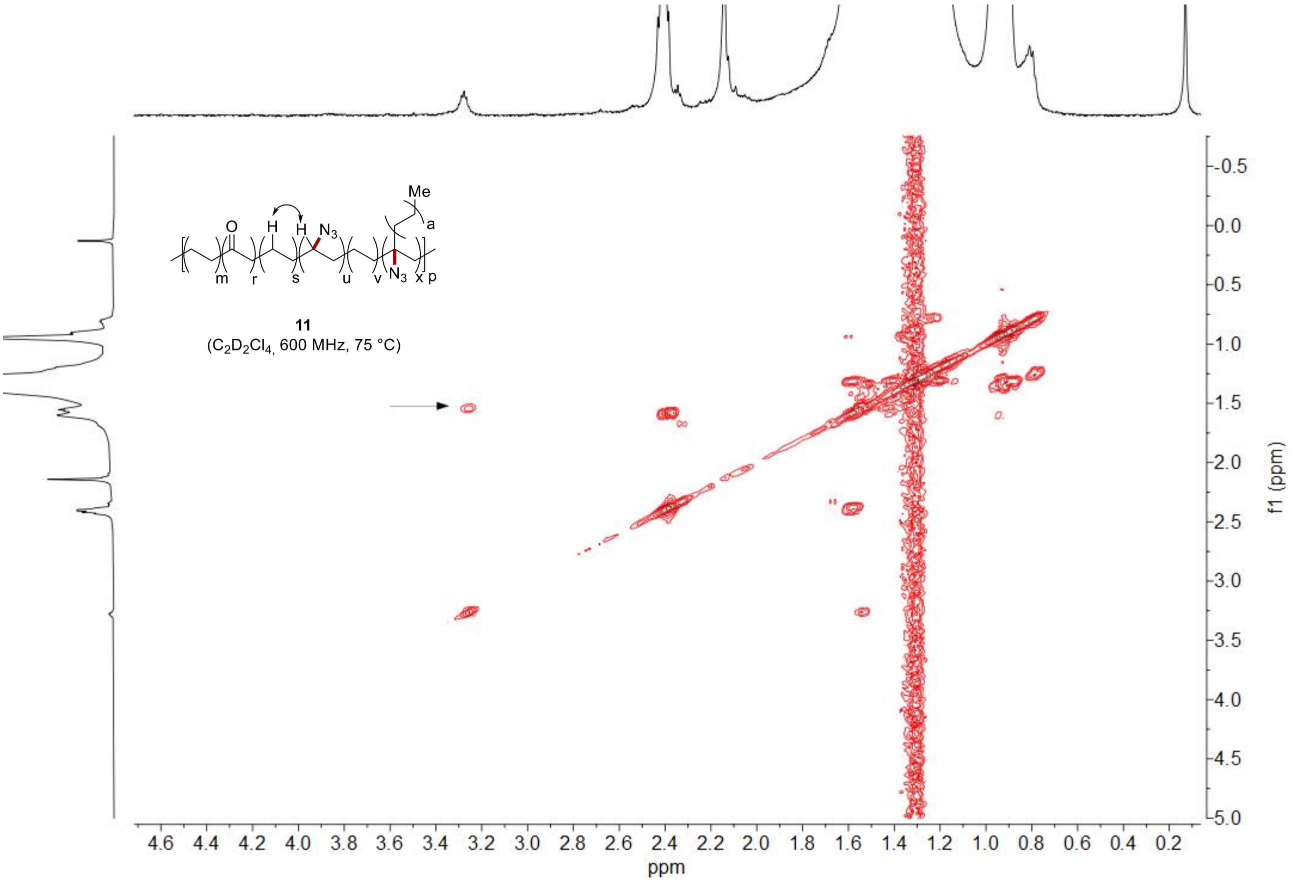


Figure S80. COSY of **11** in $C_2D_2Cl_4$ at 75 °C.

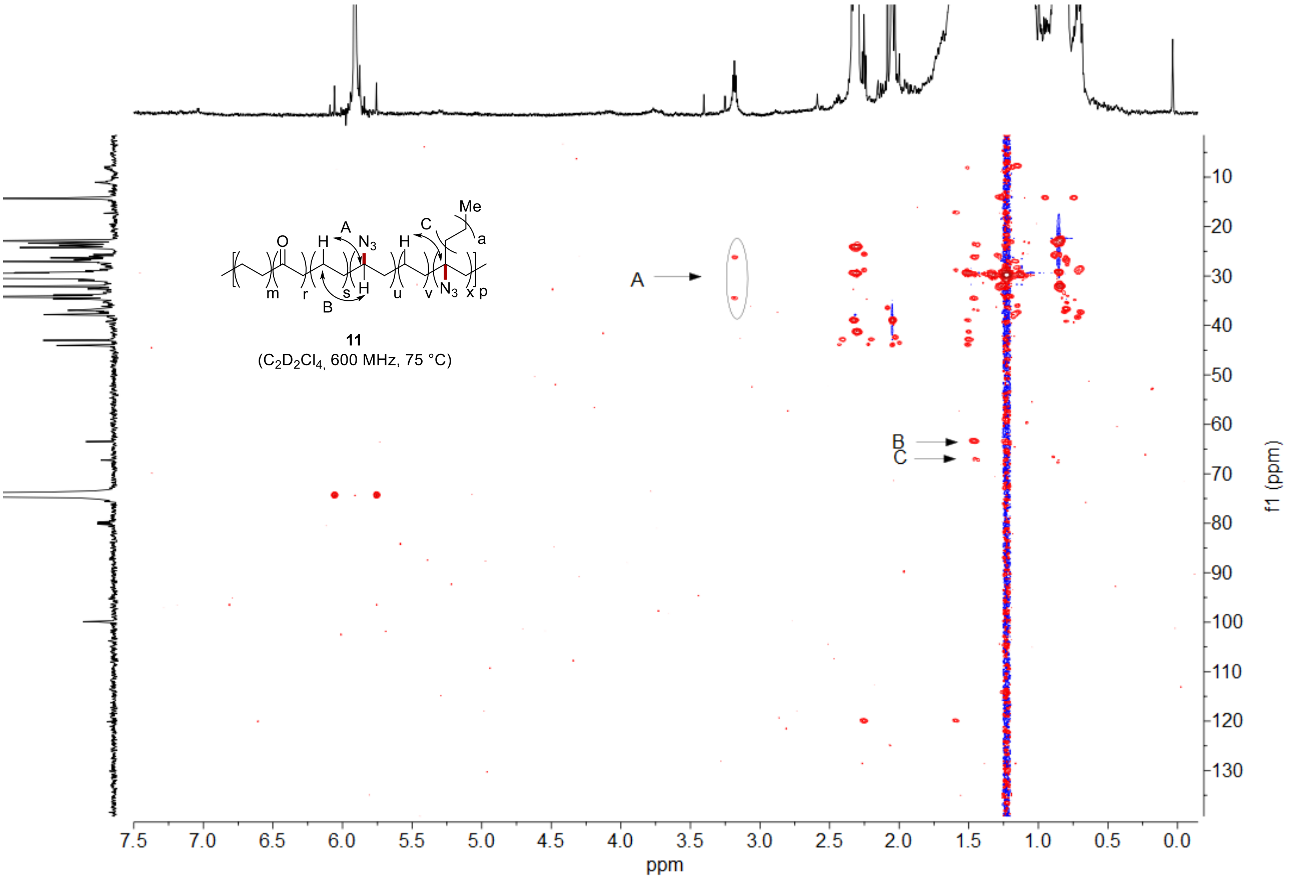


Figure S81. HMBC of **11** in $C_2D_2Cl_4$ at 75 °C.

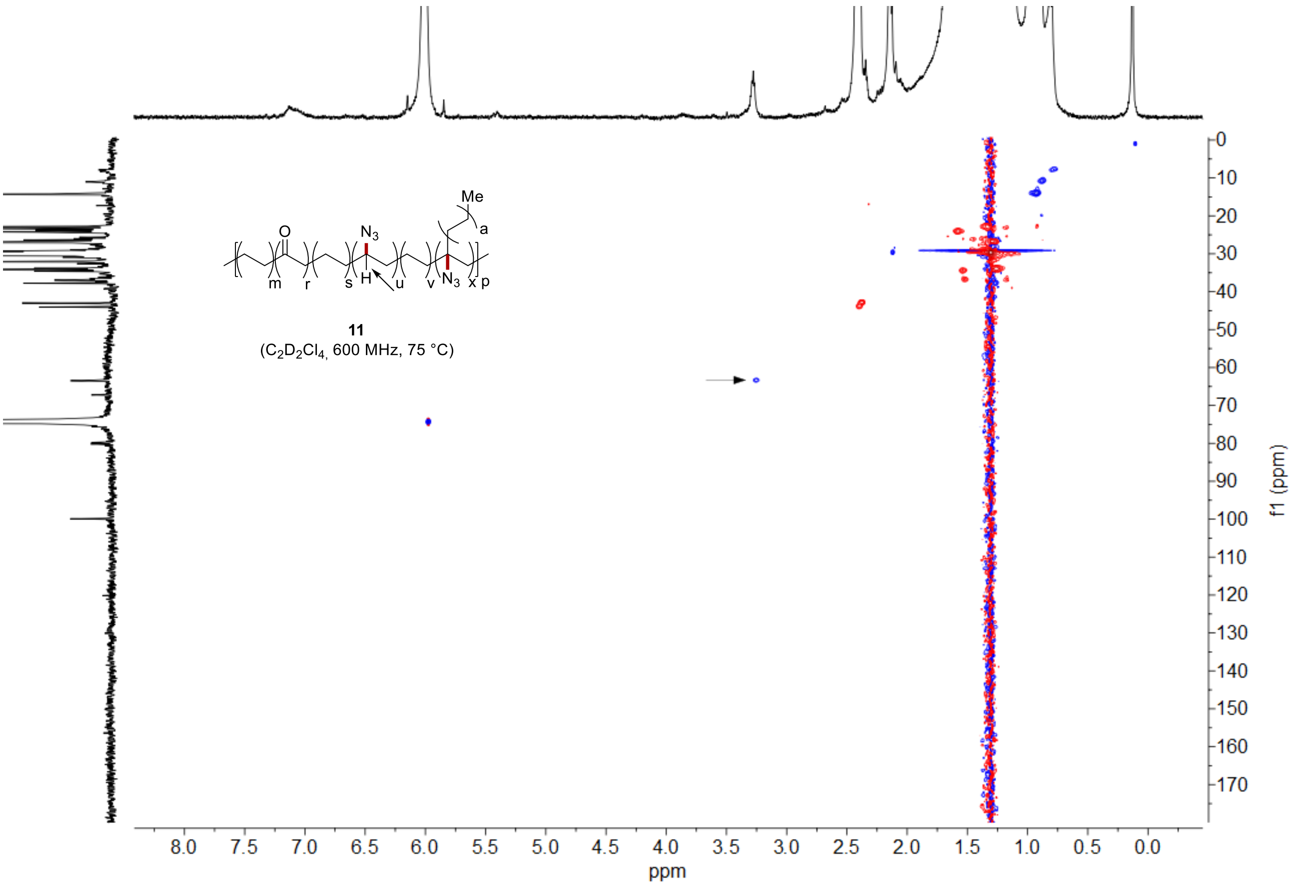


Figure S82. HSQC of **11** in $C_2D_2Cl_4$ at 75 °C.

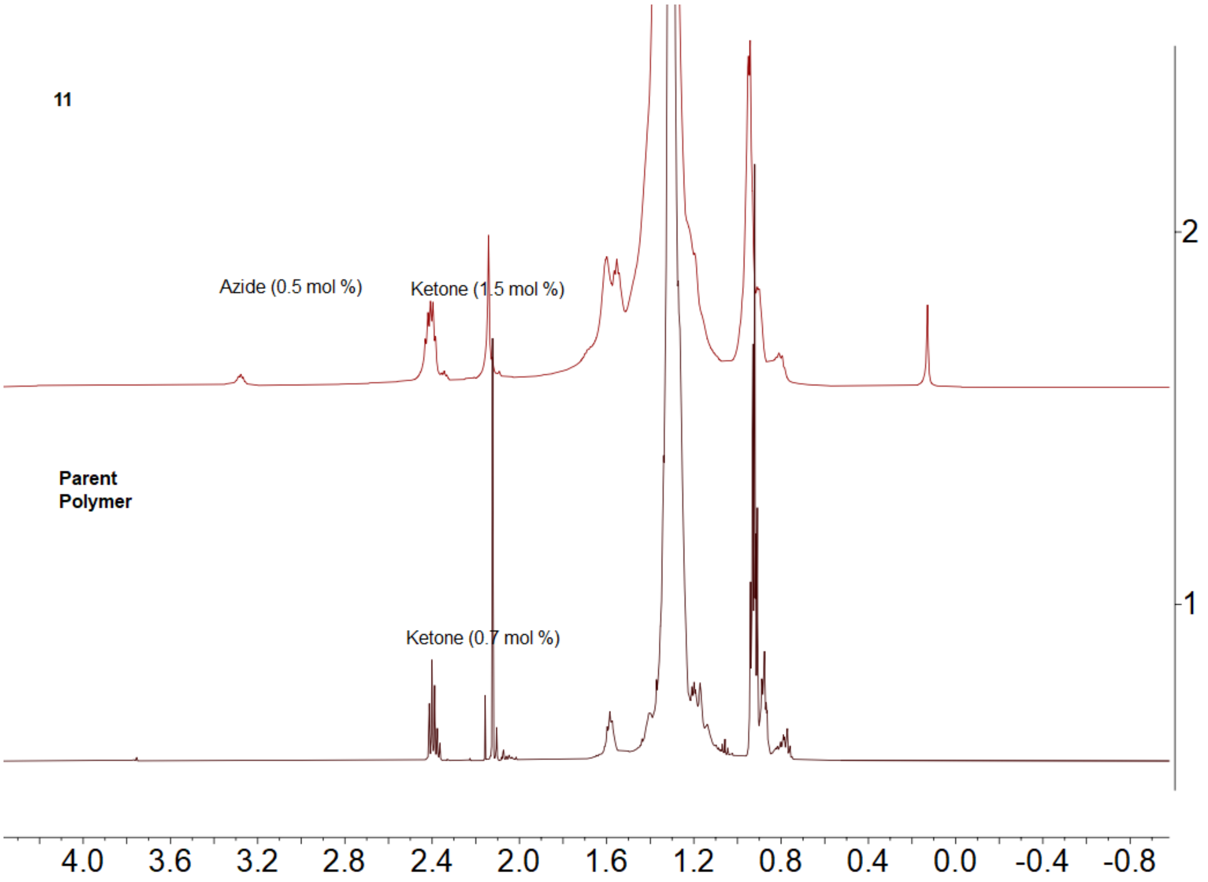


Figure S83. ^{1}H NMR **11** and parent polymer in $C_2D_2Cl_4$ at 75 °C.

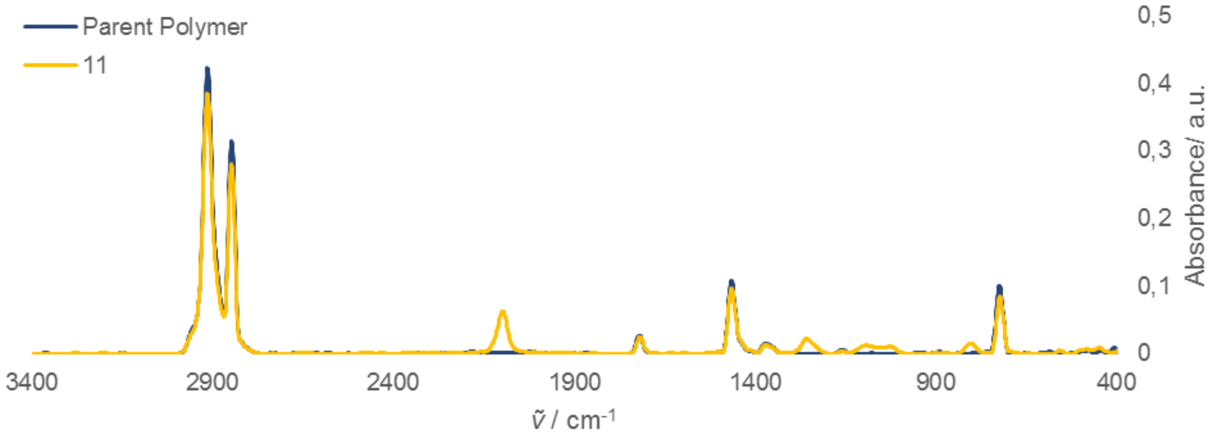


Figure S84. IR spectrum of parent (blue) and modified polymer **11** (yellow) in arbitrary units (a.u.).

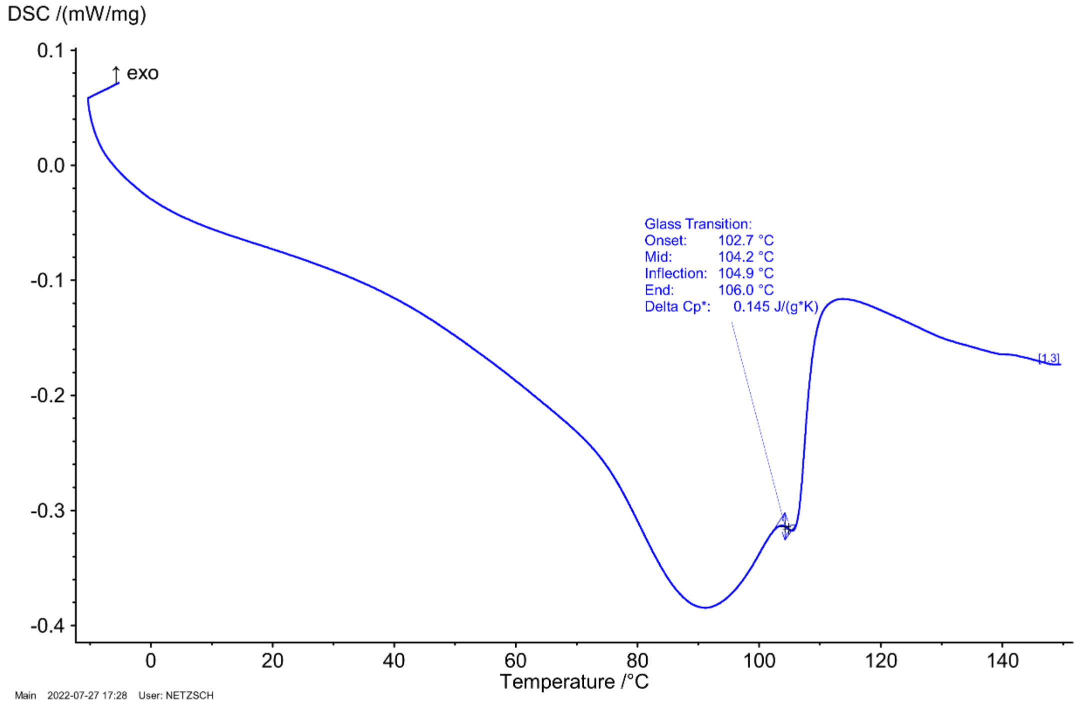


Figure S85. DSC of **11**.

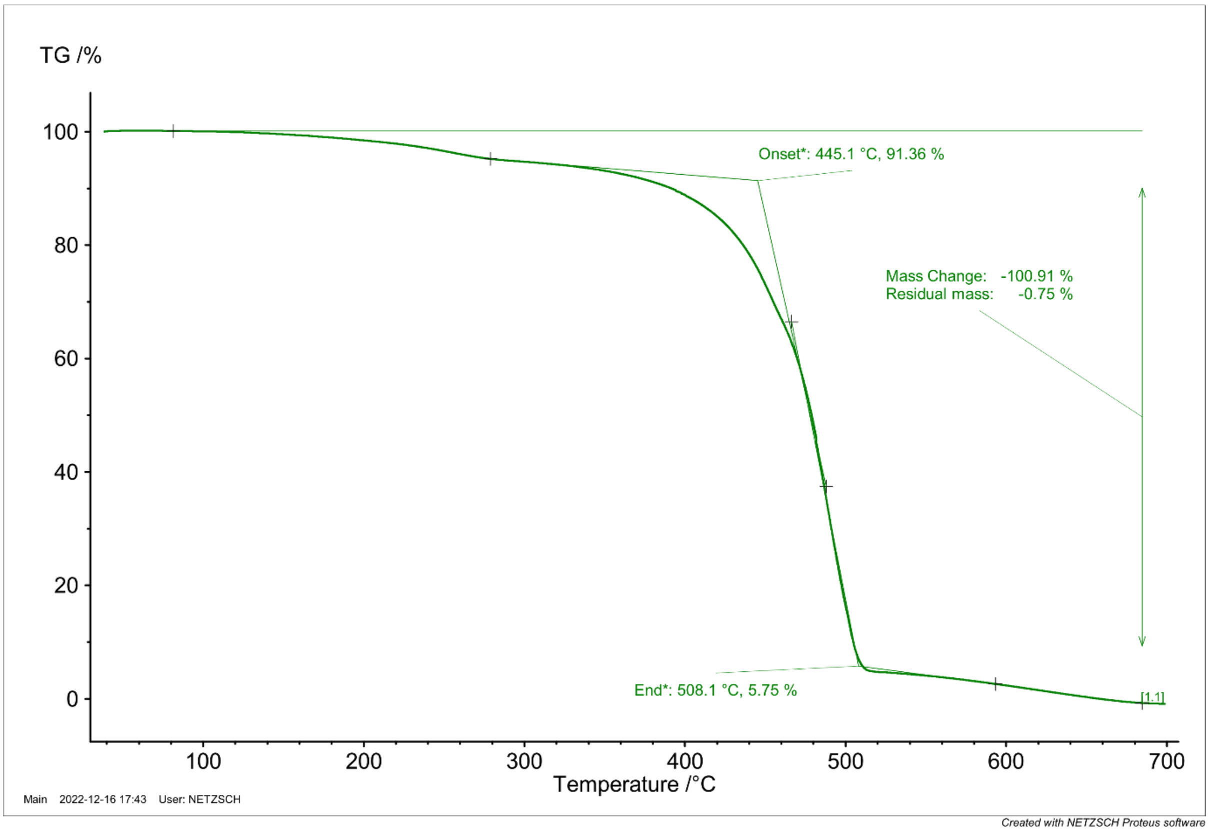


Figure S86. TGA of **11**.

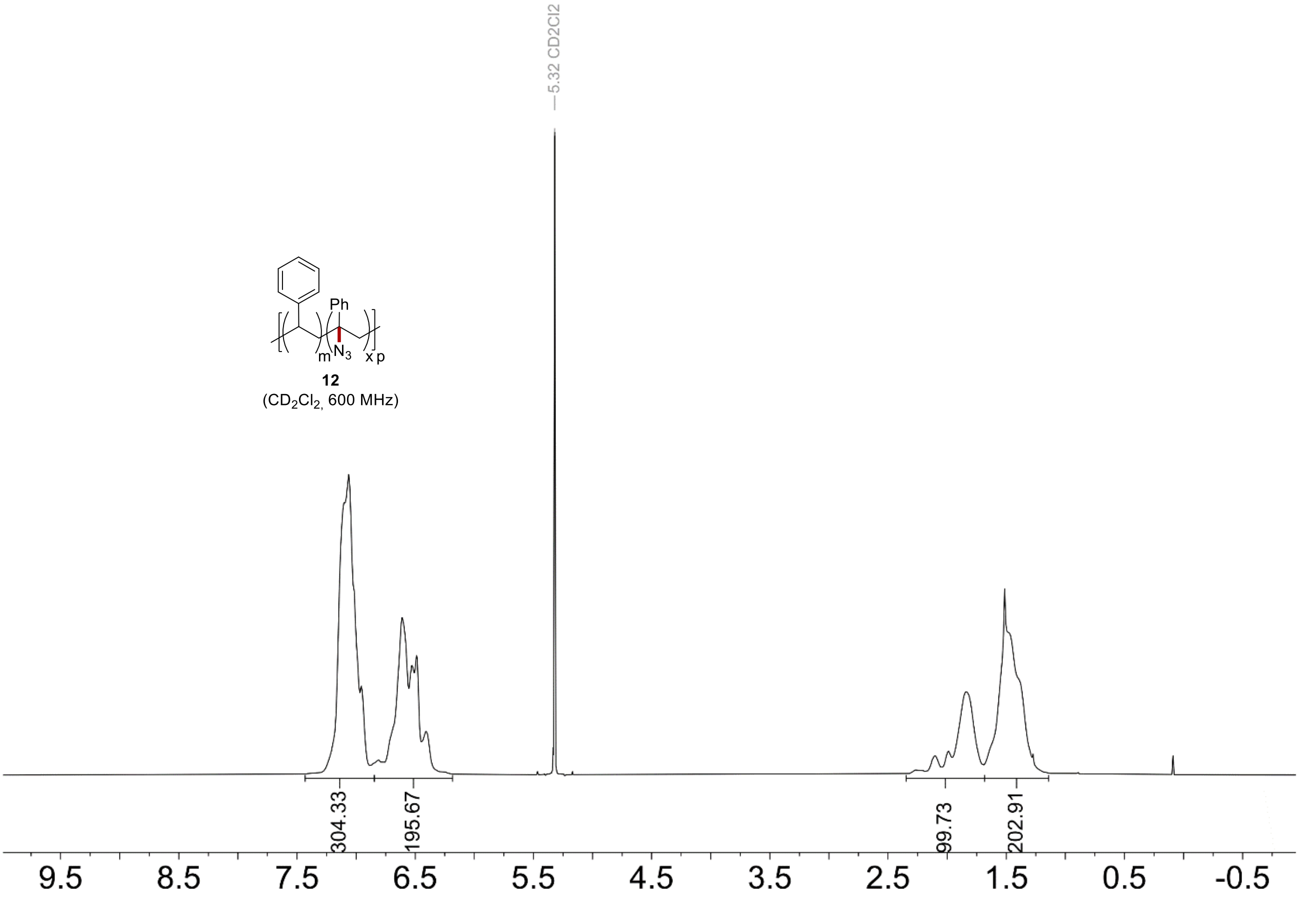


Figure S87. ^{1}H NMR of **12** in CD_2Cl_2.

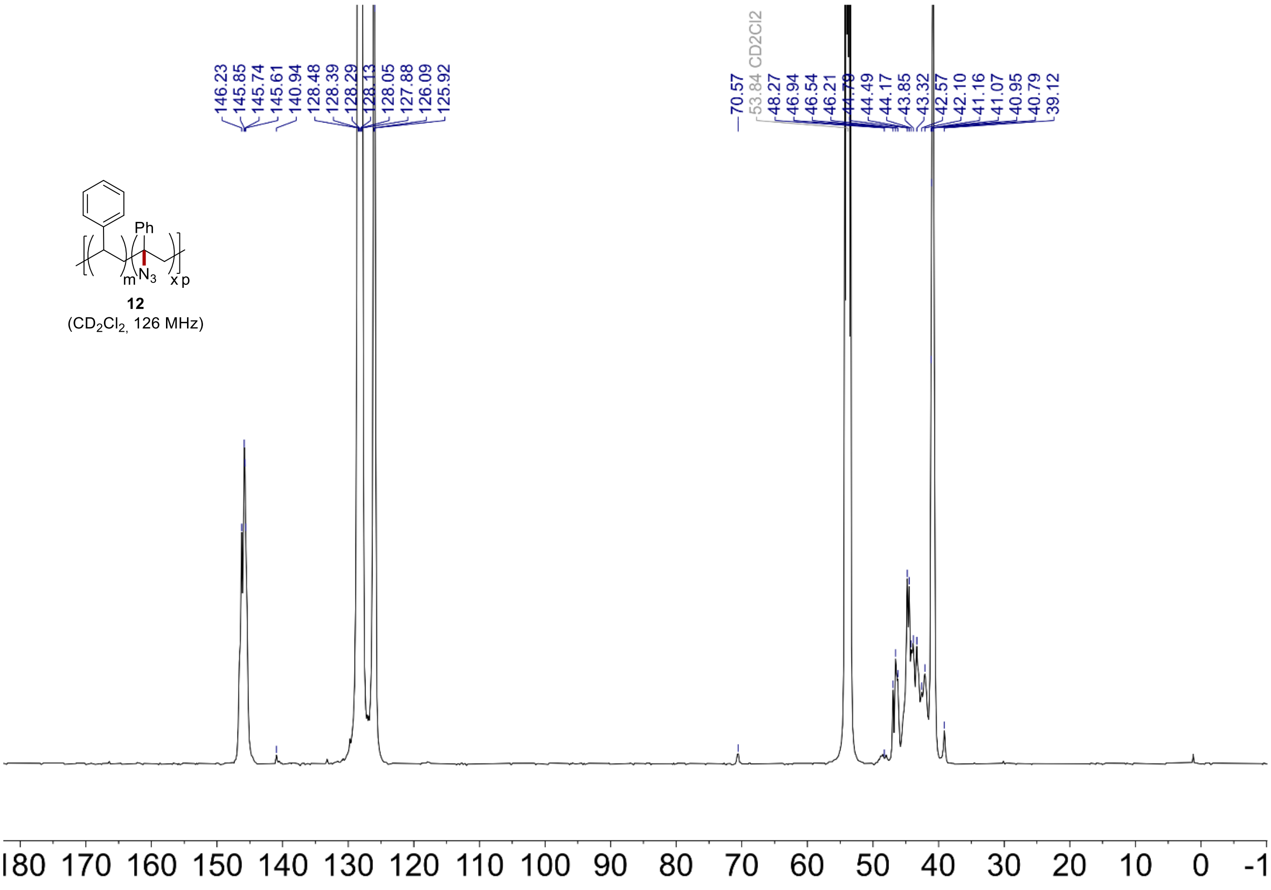


Figure S88. ^{13}C NMR of **12** in CD_2Cl_2.

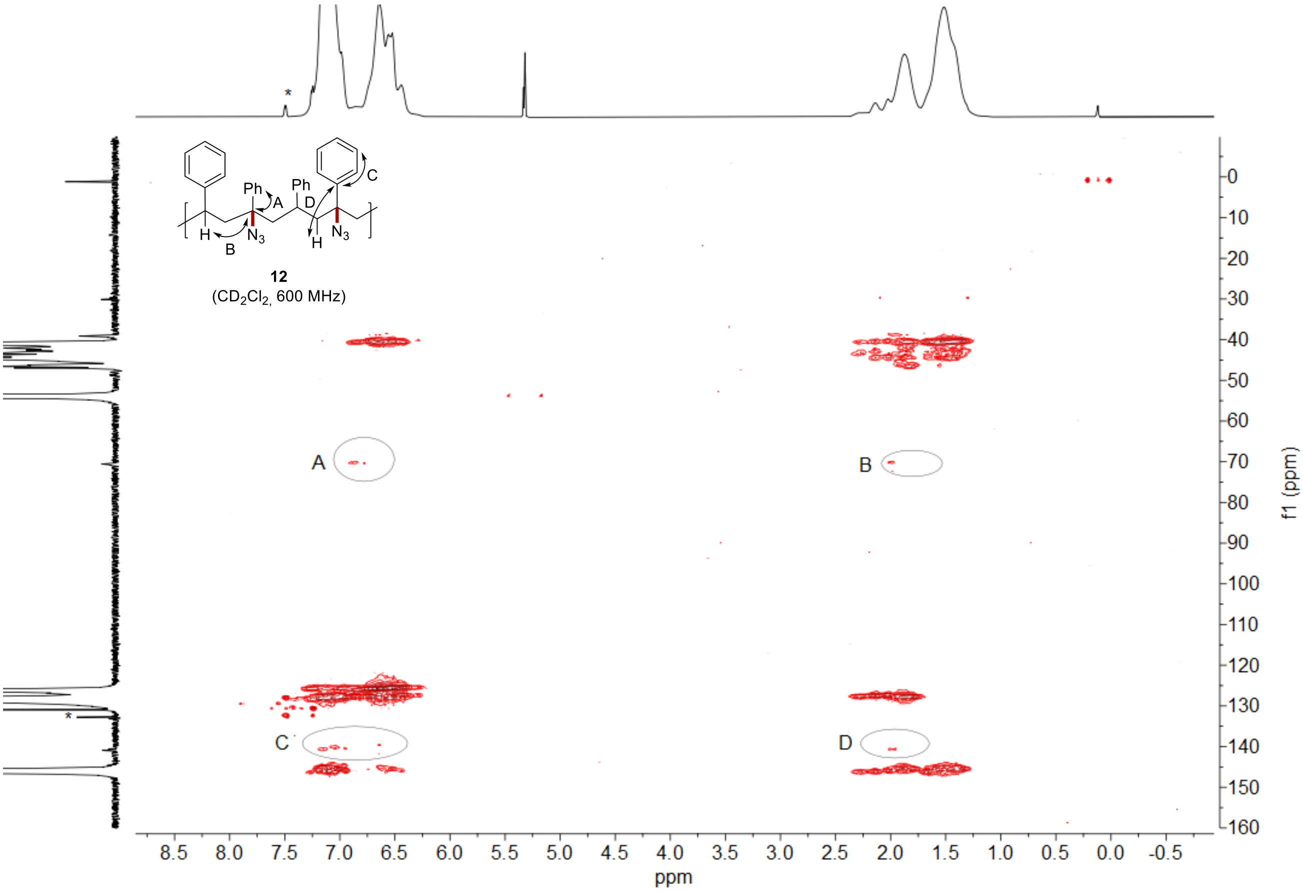


Figure S89. HMBC NMR of **12** in CD_2Cl_2. Asterisk marks 1,2-DCB impurities.

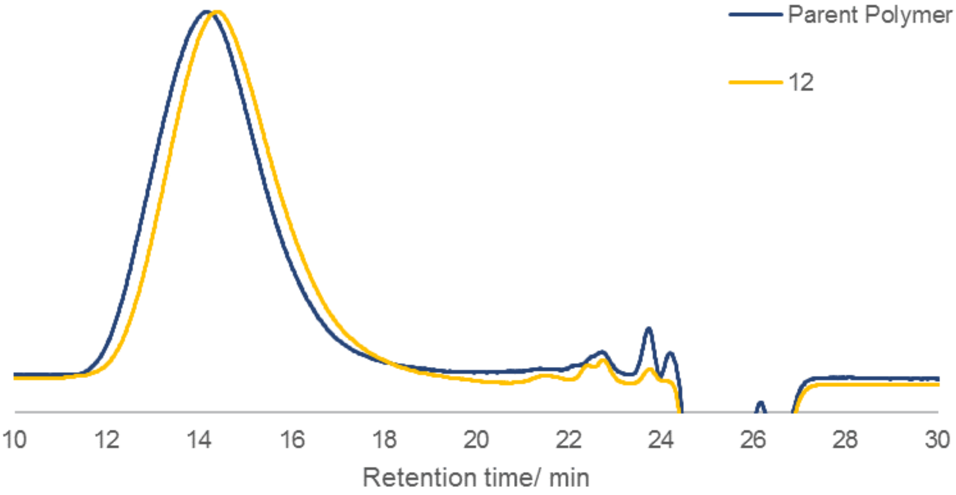


Figure S90. Normalized chromatogram of parent (blue) and modified polymer **12** (yellow).

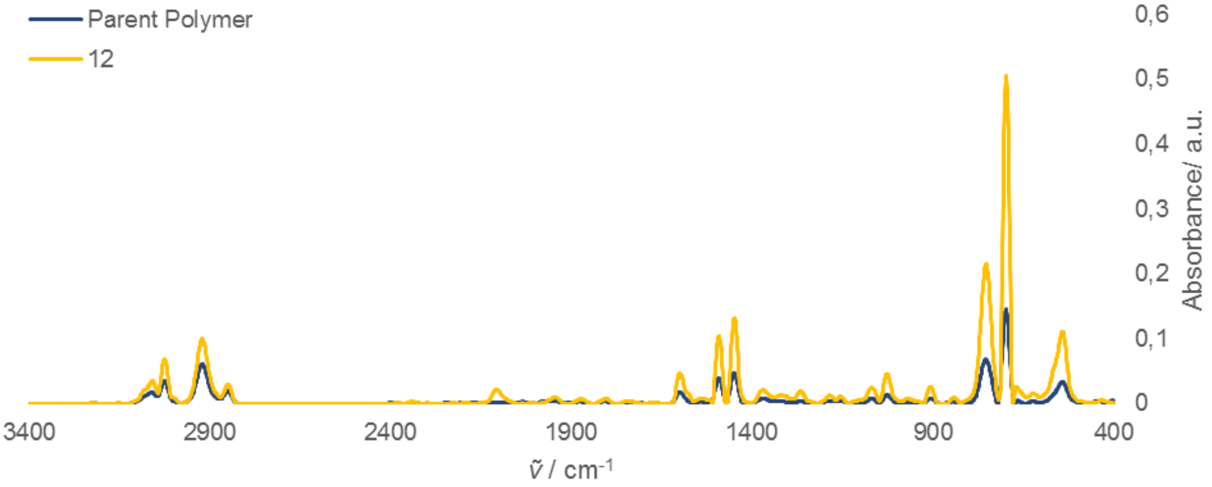


Figure S91. IR spectrum of parent (blue) and modified polymer **12** (yellow) in arbitrary units (a.u.).

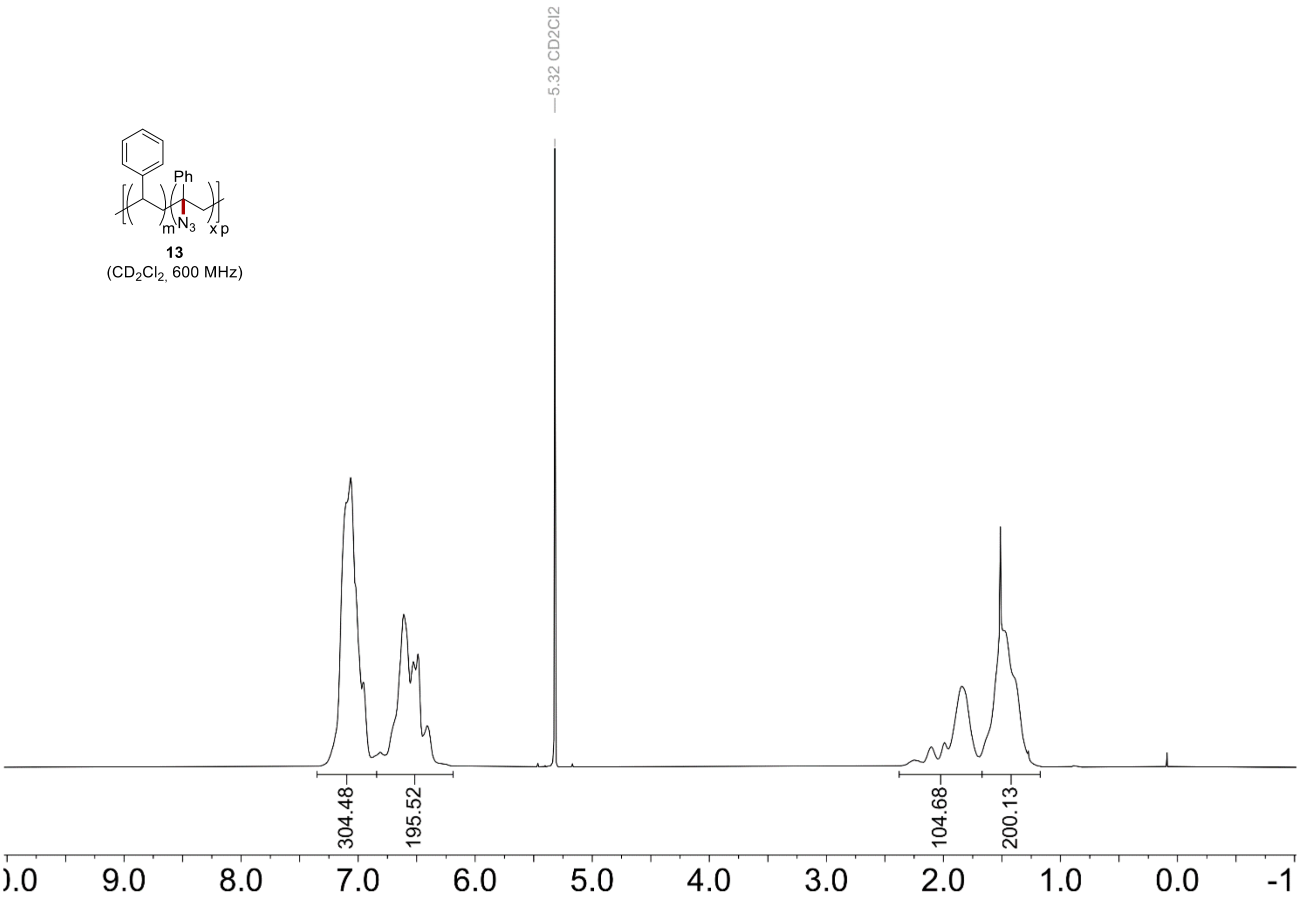


Figure S92. ^{1}H NMR of **13** in CD_2Cl_2.

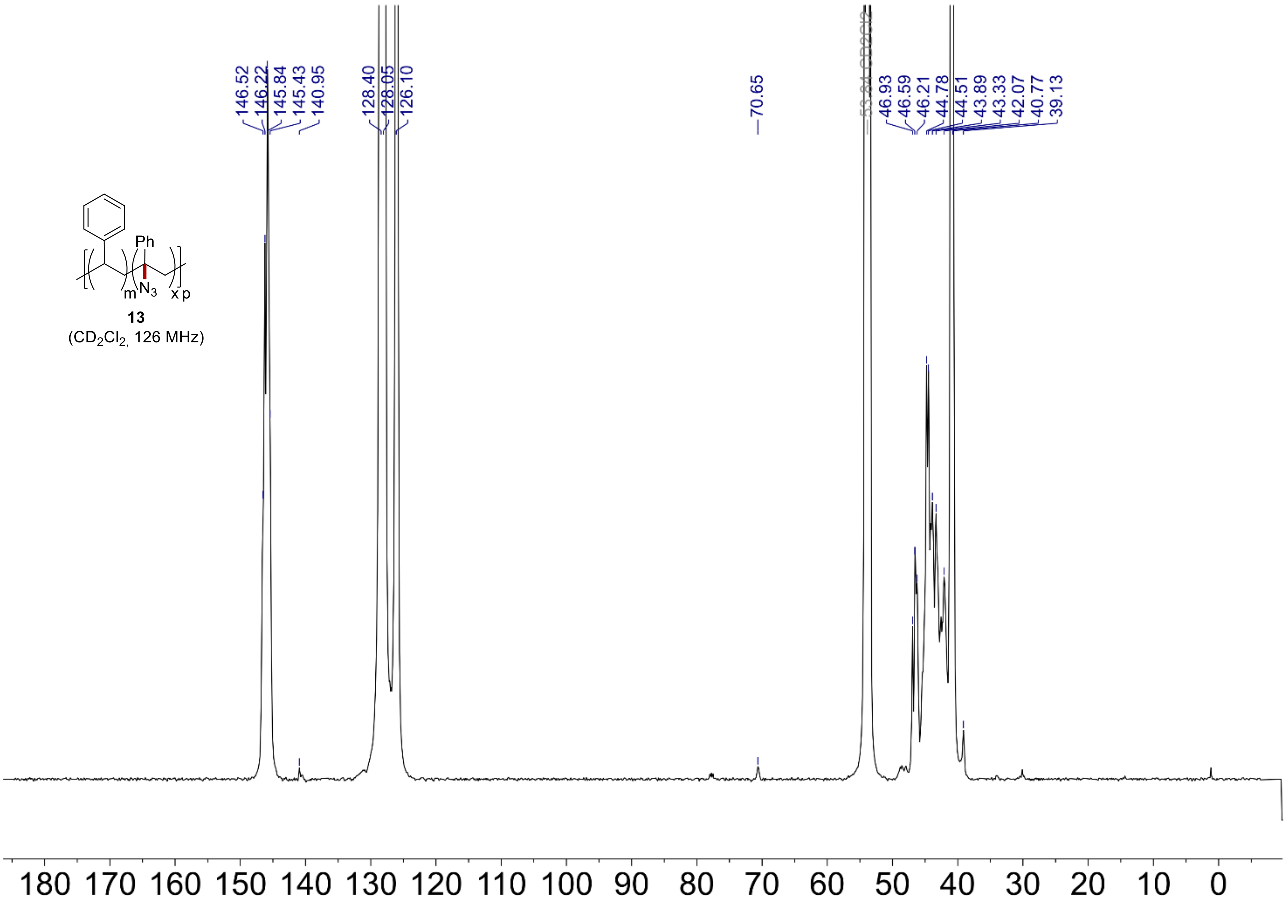


Figure S93. ^{13}C NMR of **13** in CD_2Cl_2.

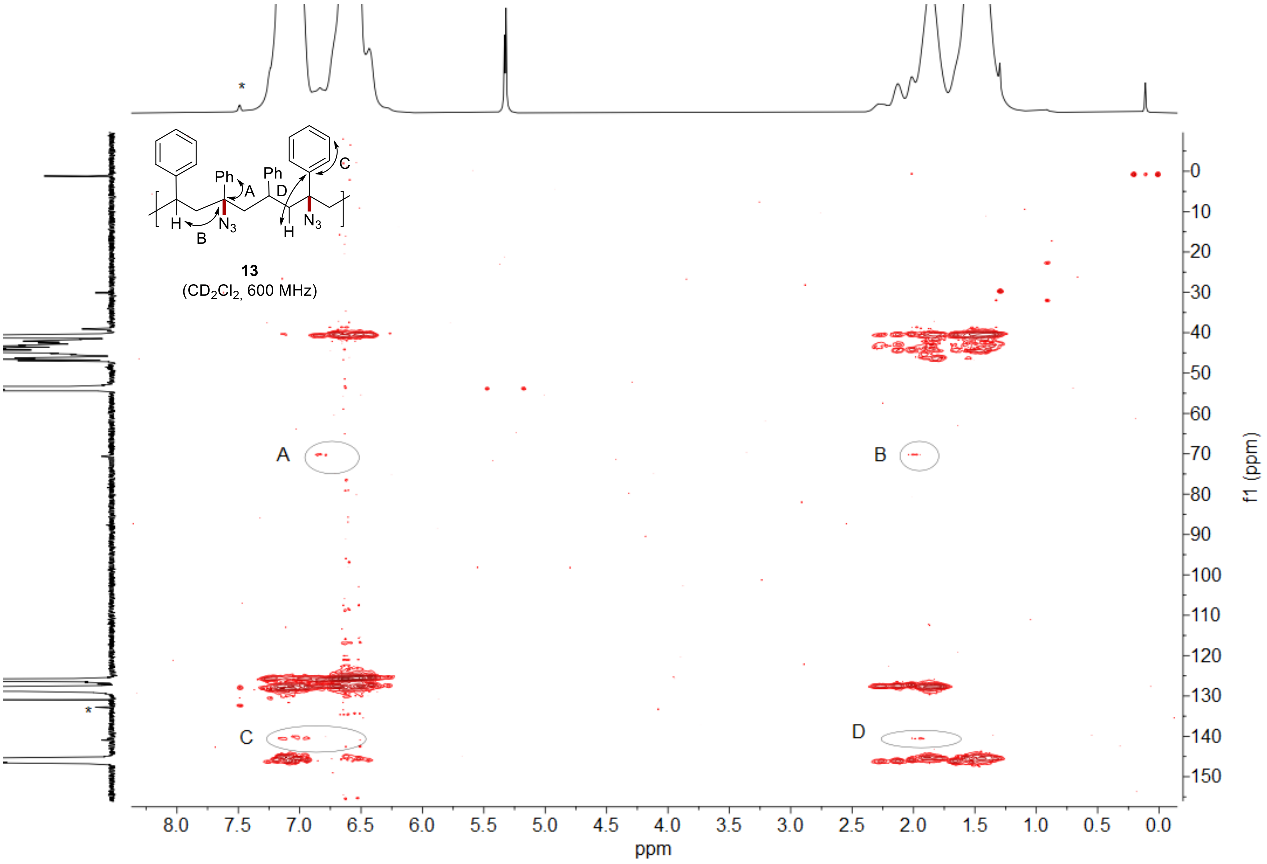


Figure S94. ^{1}H NMR of **13** in CD_2Cl_2. Asterisk marks 1,2-DCB impurities.

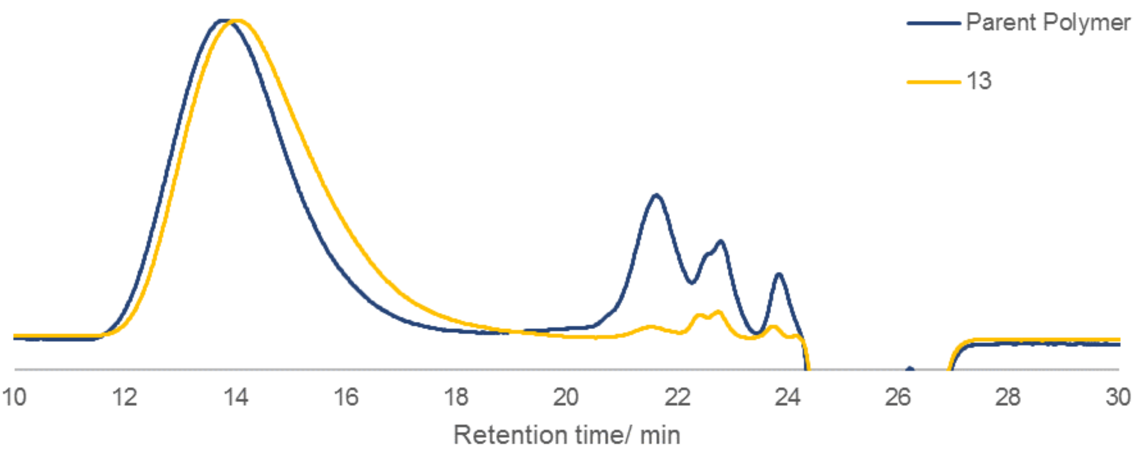


Figure S95. Normalized chromatogram of parent (blue) and modified polymer **13** (yellow).

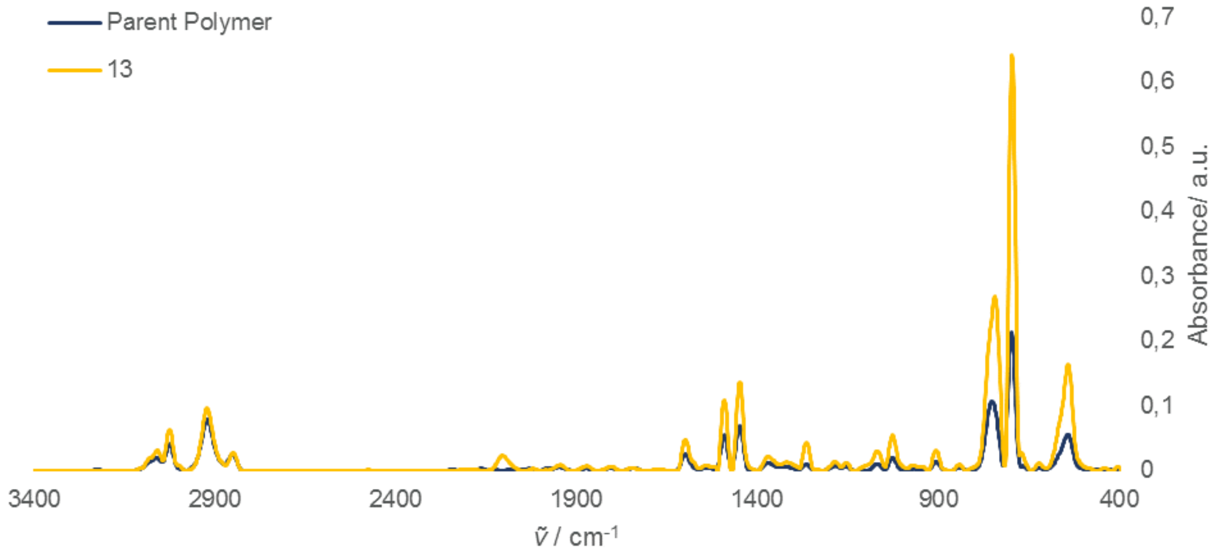


Figure S96. IR spectrum of parent (blue) and modified polymer **13** (yellow) in arbitrary units (a.u.).

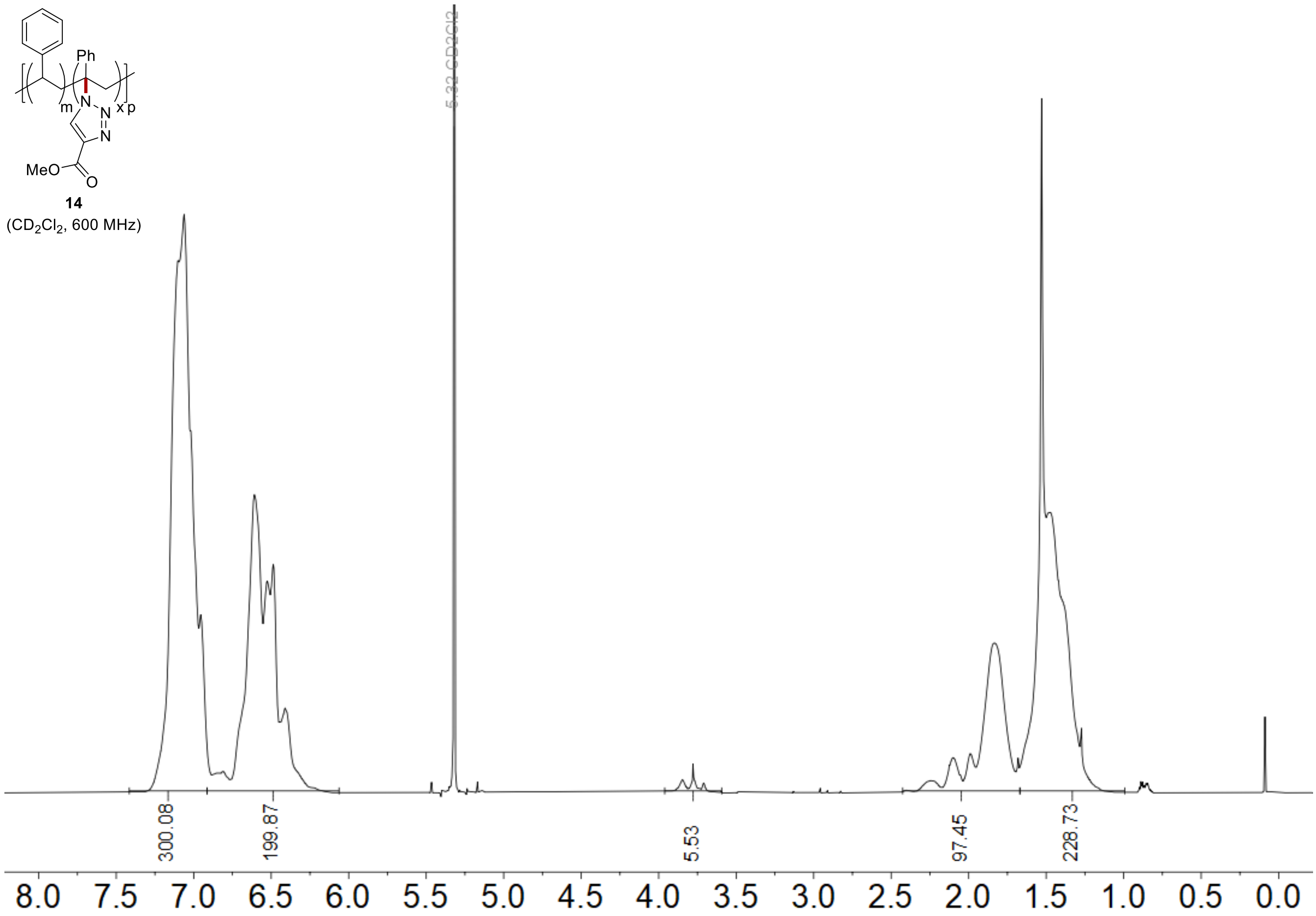


Figure S97. ^{1}H NMR of **14** in CD_2Cl_2.

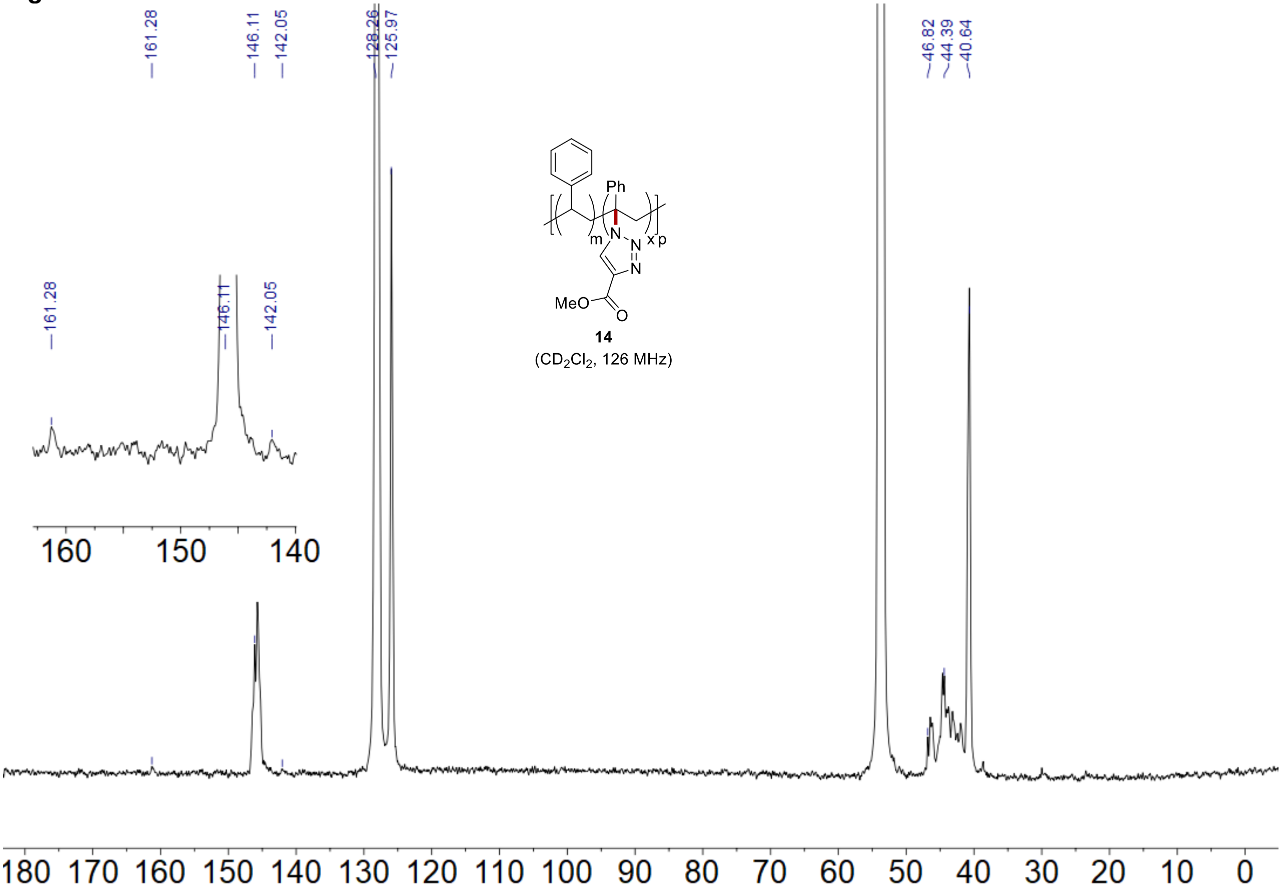


Figure S98. ^{13}C NMR of **14** in CD_2Cl_2.

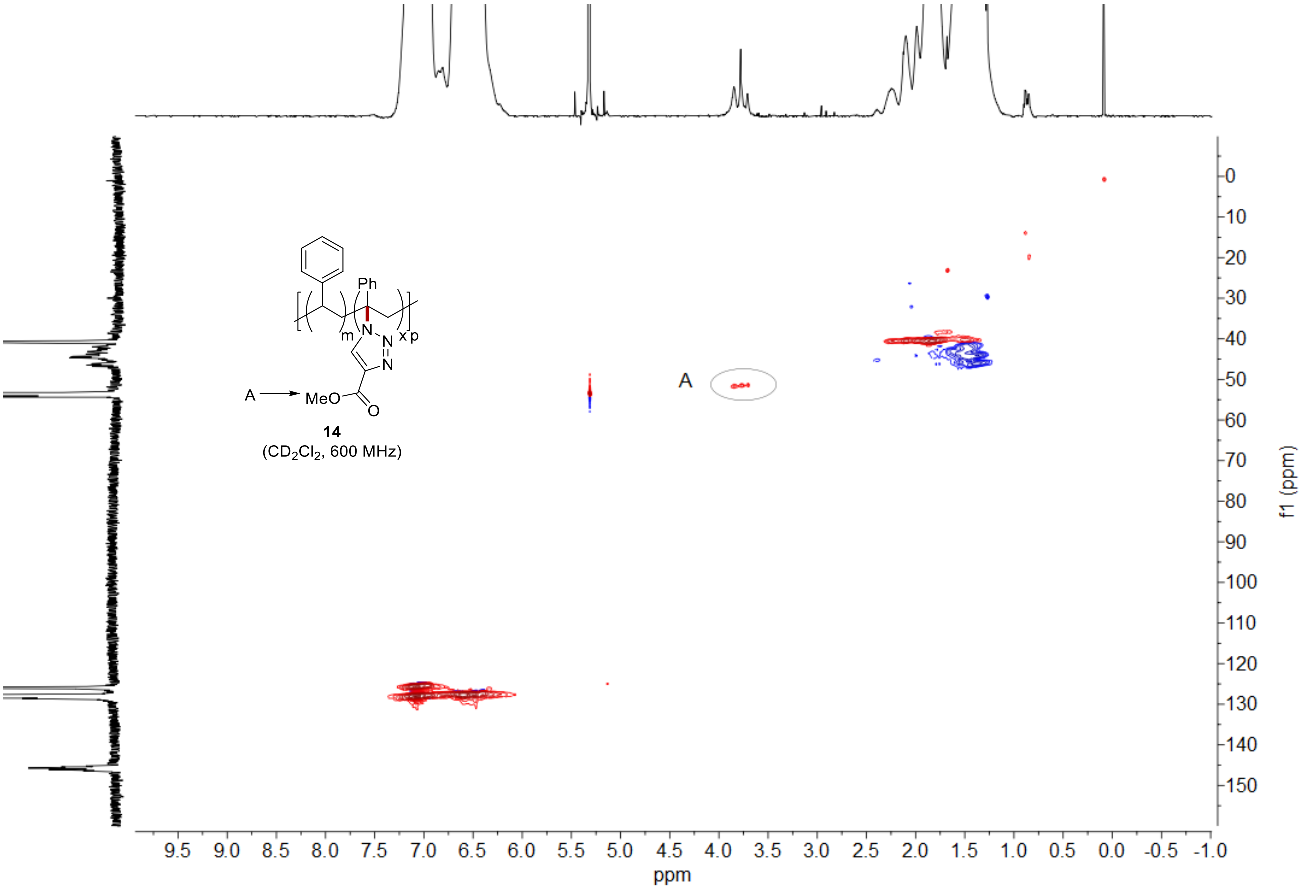


Figure S99. HSQC of **14** in CD_2Cl_2.

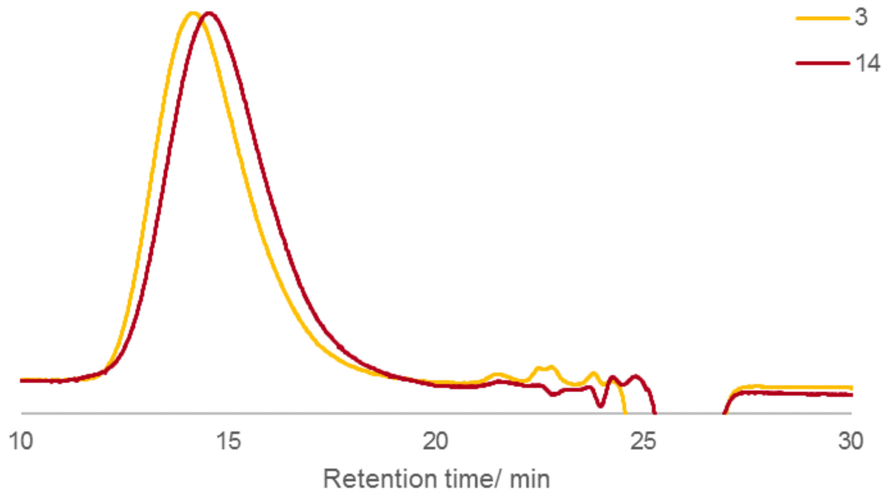


Figure S100. Normalized chromatogram of **3** (yellow) and modified polymer **14** (red).

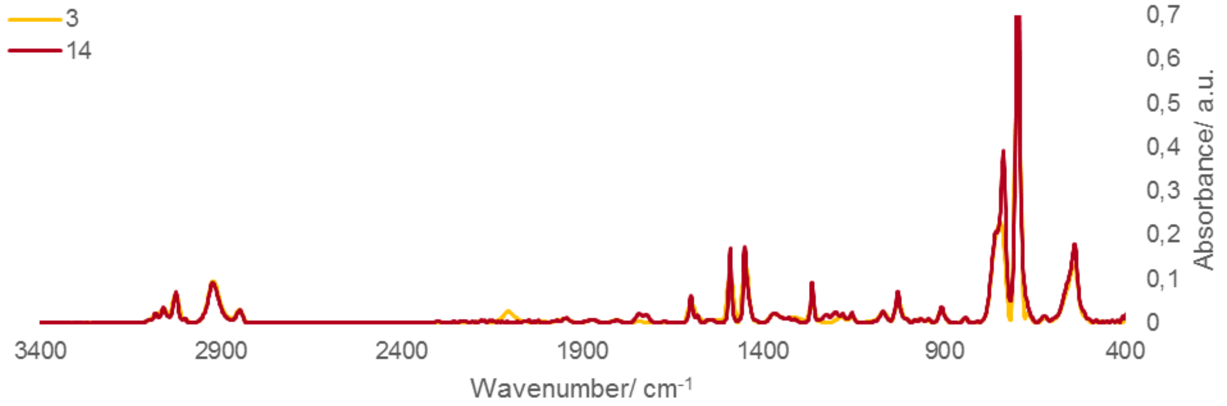


Figure S101. IR spectrum of azide polymer **3** (yellow) and 1,3-cycloaddition product **14** (red) in arbitrary units (a.u.).

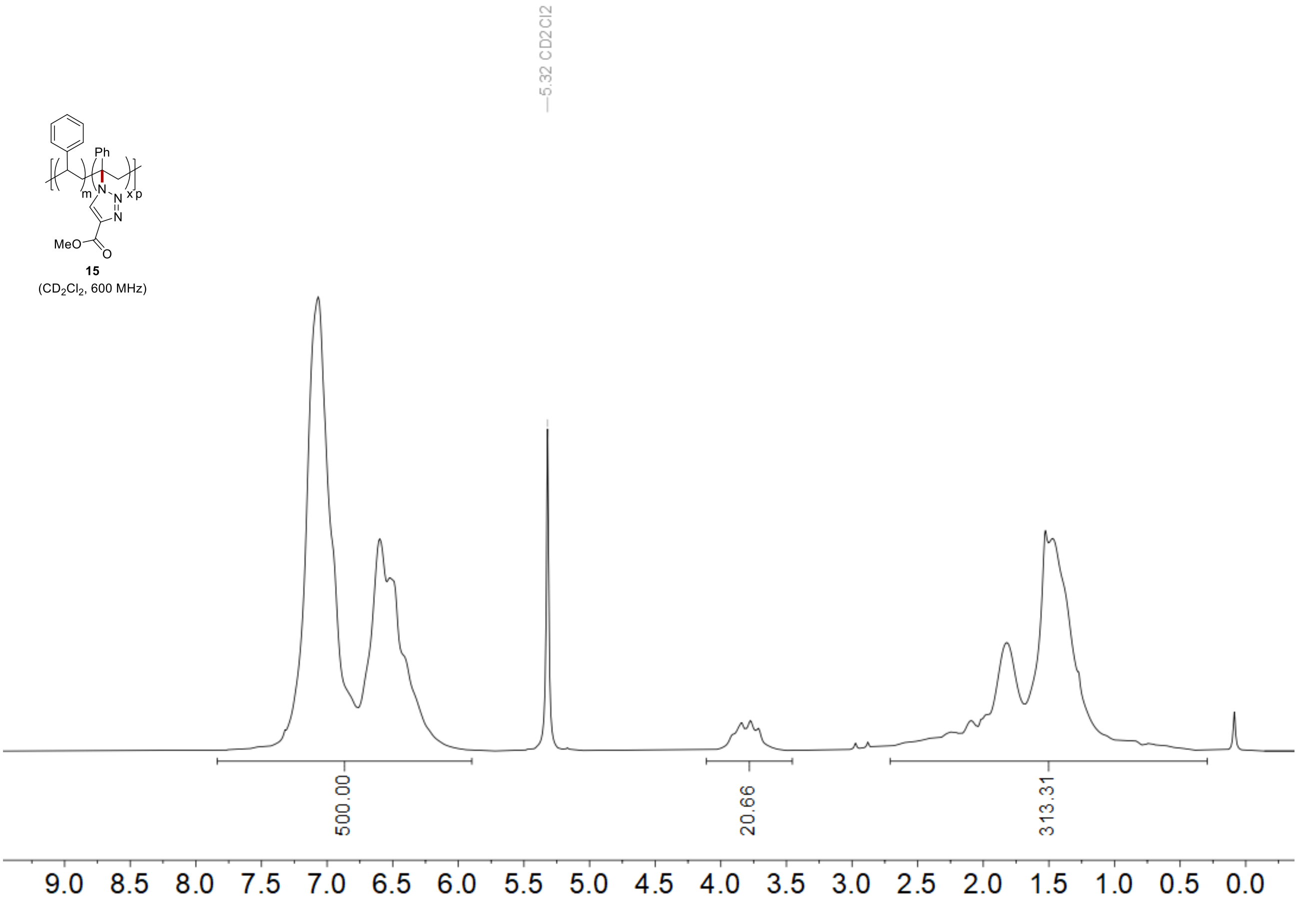


Figure S102. ^{1}H NMR of **15** in CD_2Cl_2.

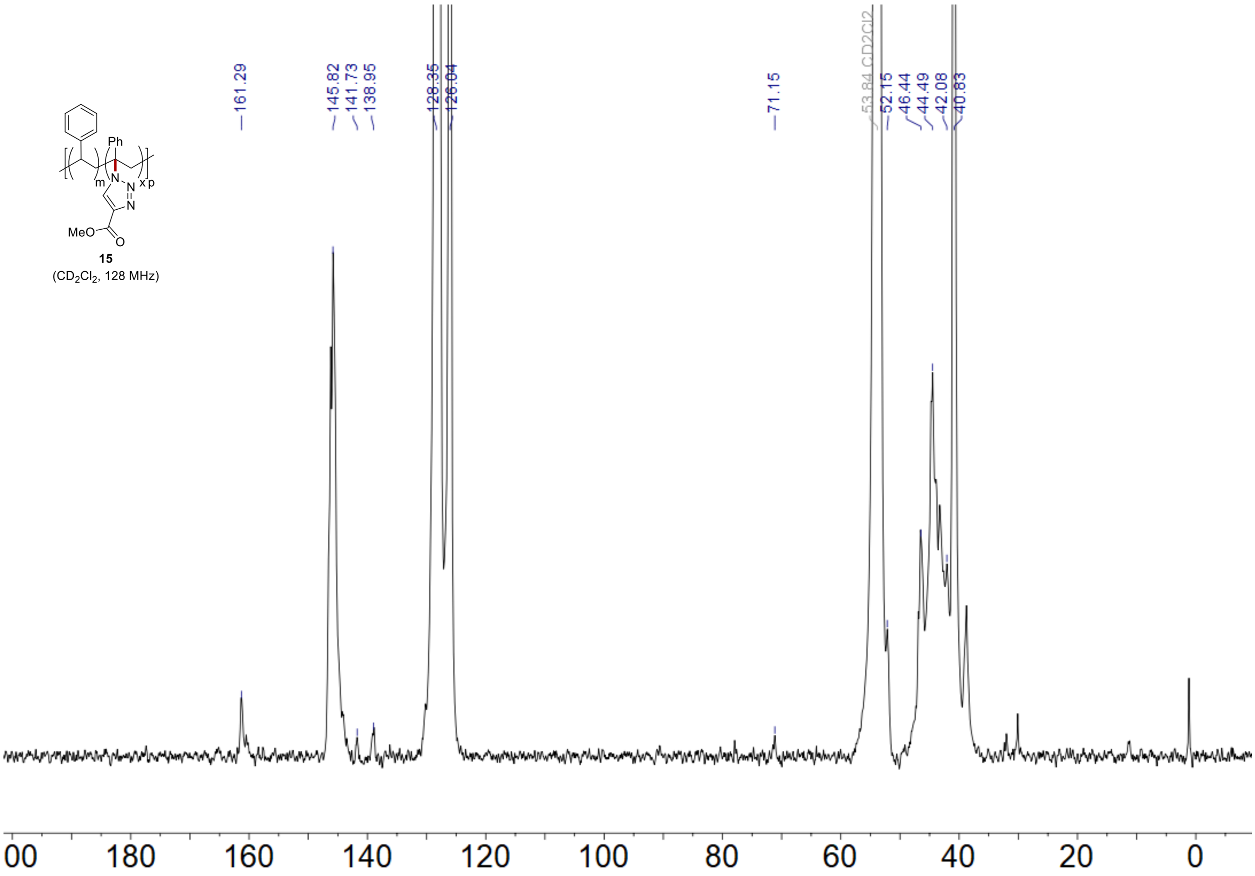


Figure S103. ^{13}C NMR of **15** in CD_2Cl_2.

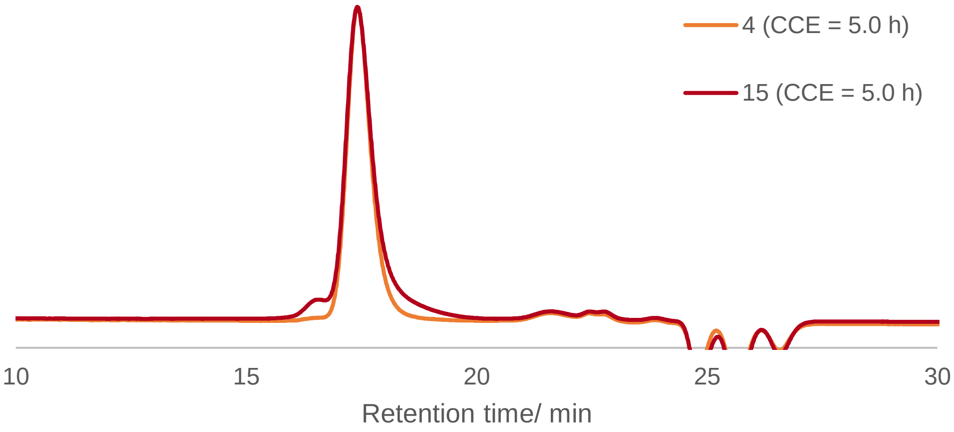


Figure S104. Normalized chromatogram of **4** after 5.0 h of CCE (orange) and modified polymer **15** (red).

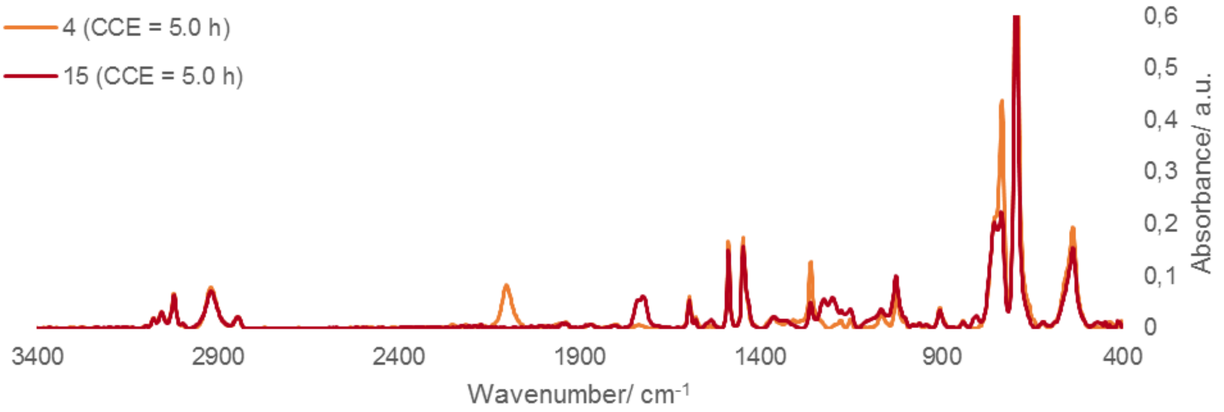


Figure S105. IR spectrum of **4** after 5.0 h of CCE (orange) and modified polymer **15** (red) in arbitrary units (a.u.).

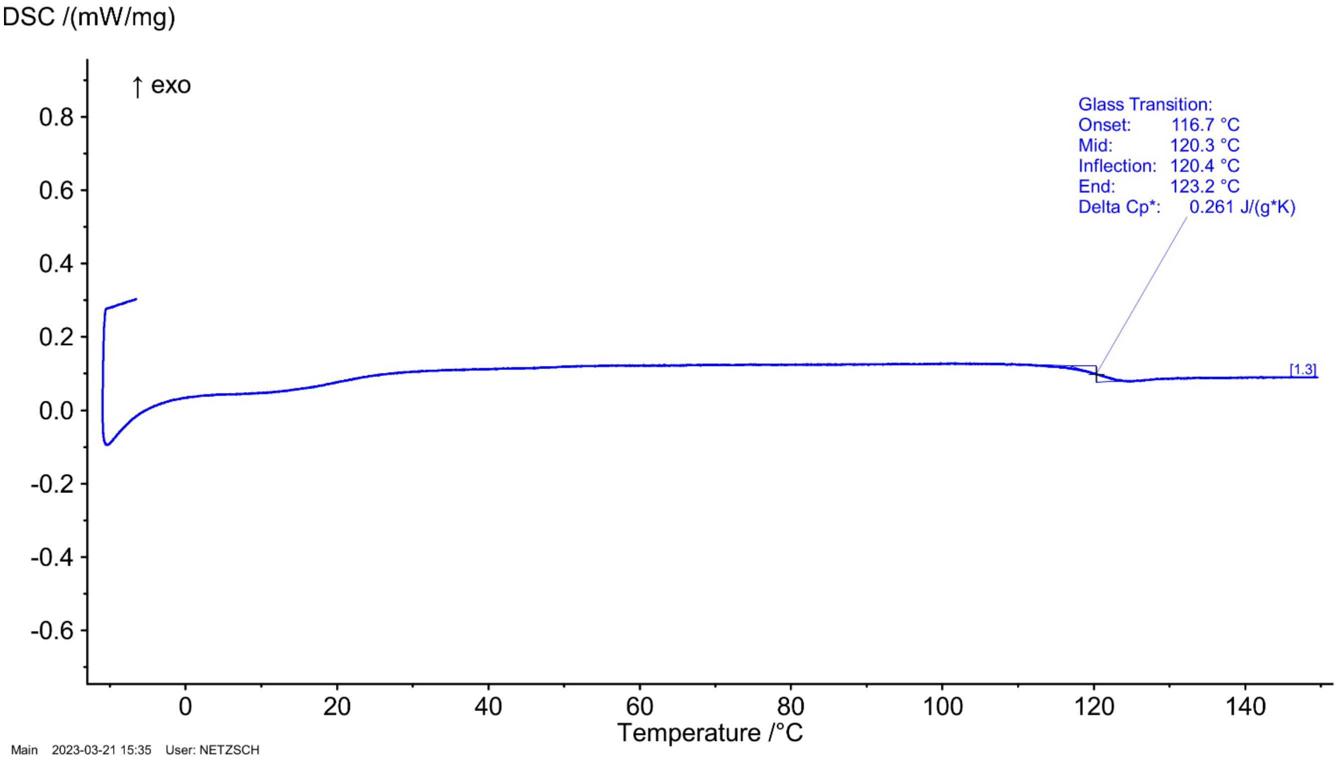


Figure S106. DSC of **15**.

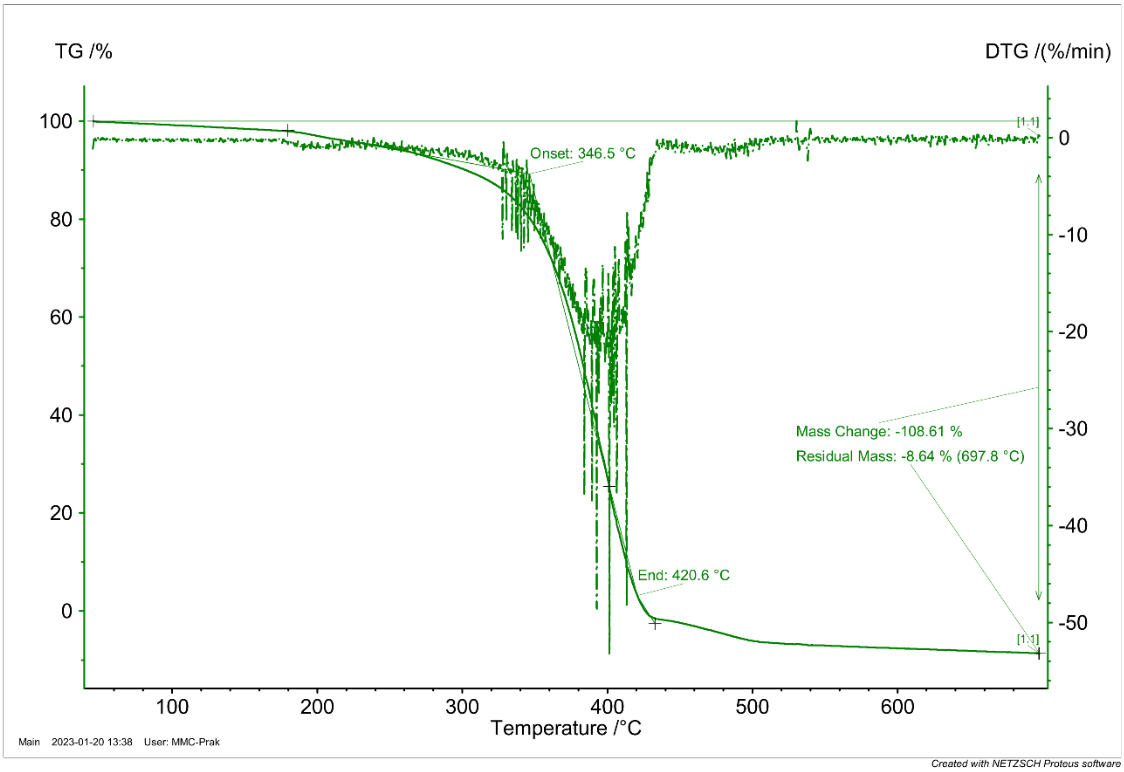


Figure S107. TGA of **15**.

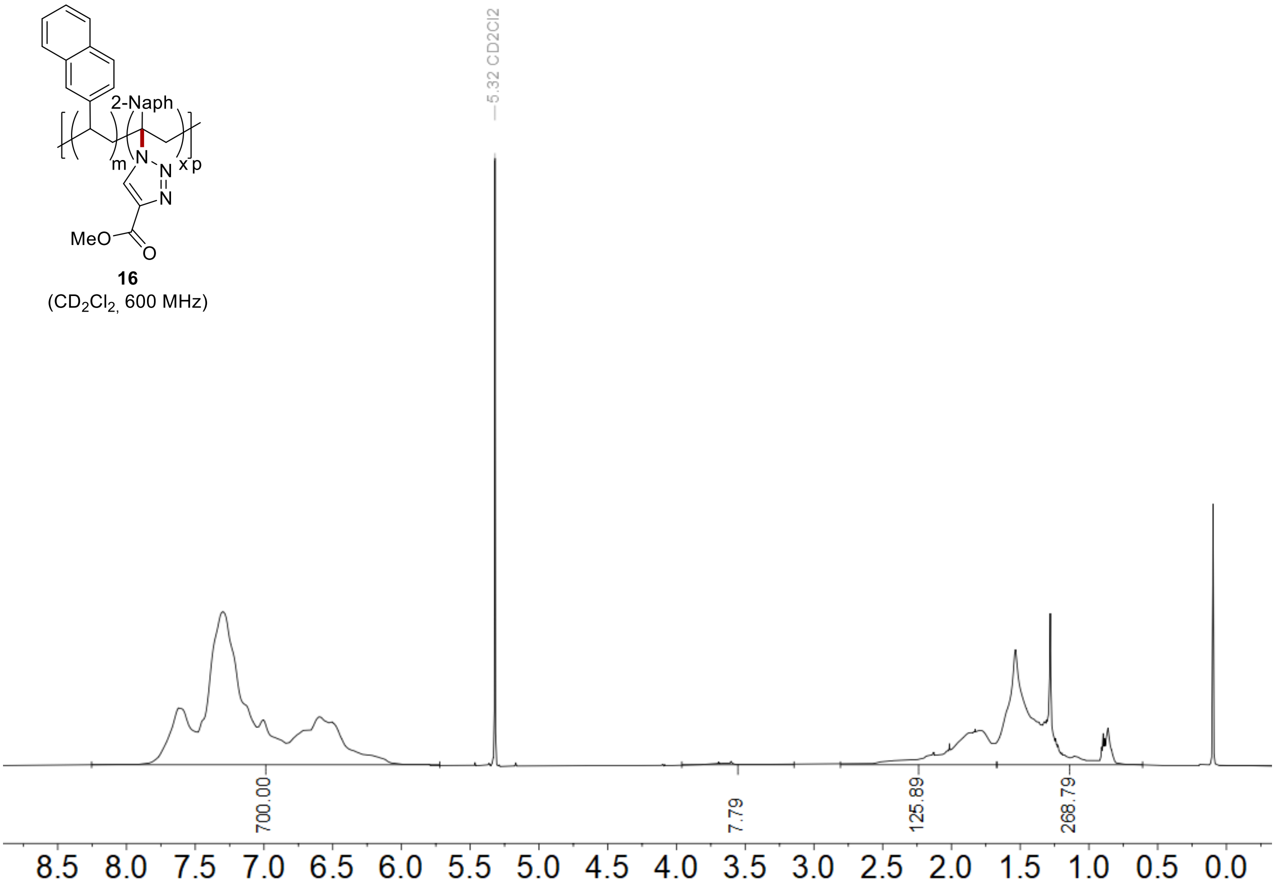


Figure S108. ^{1}H NMR of **16** in CD_2Cl_2.

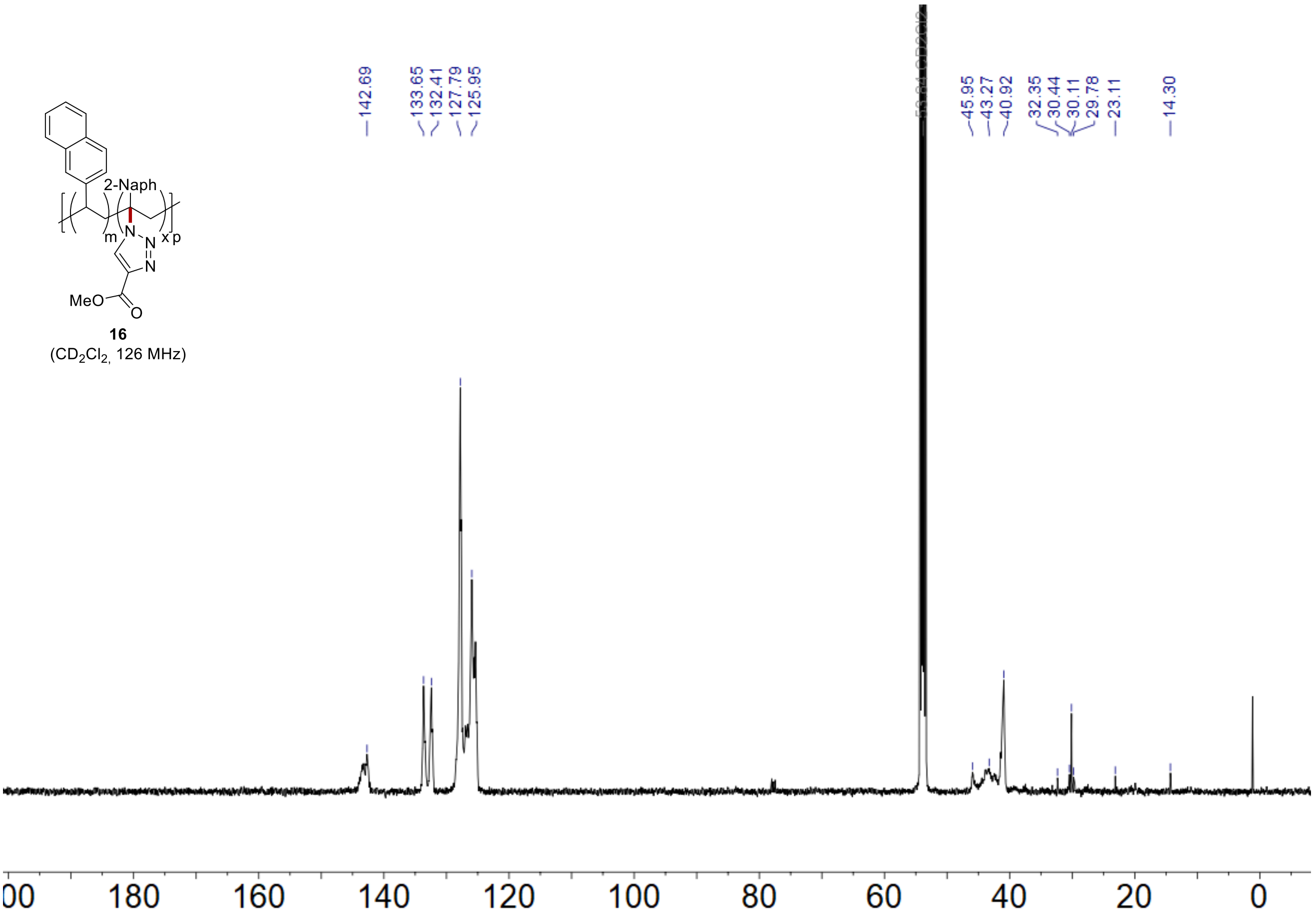


Figure S109. ^{13}C NMR of **16** in CD$_2$Cl$_2$.

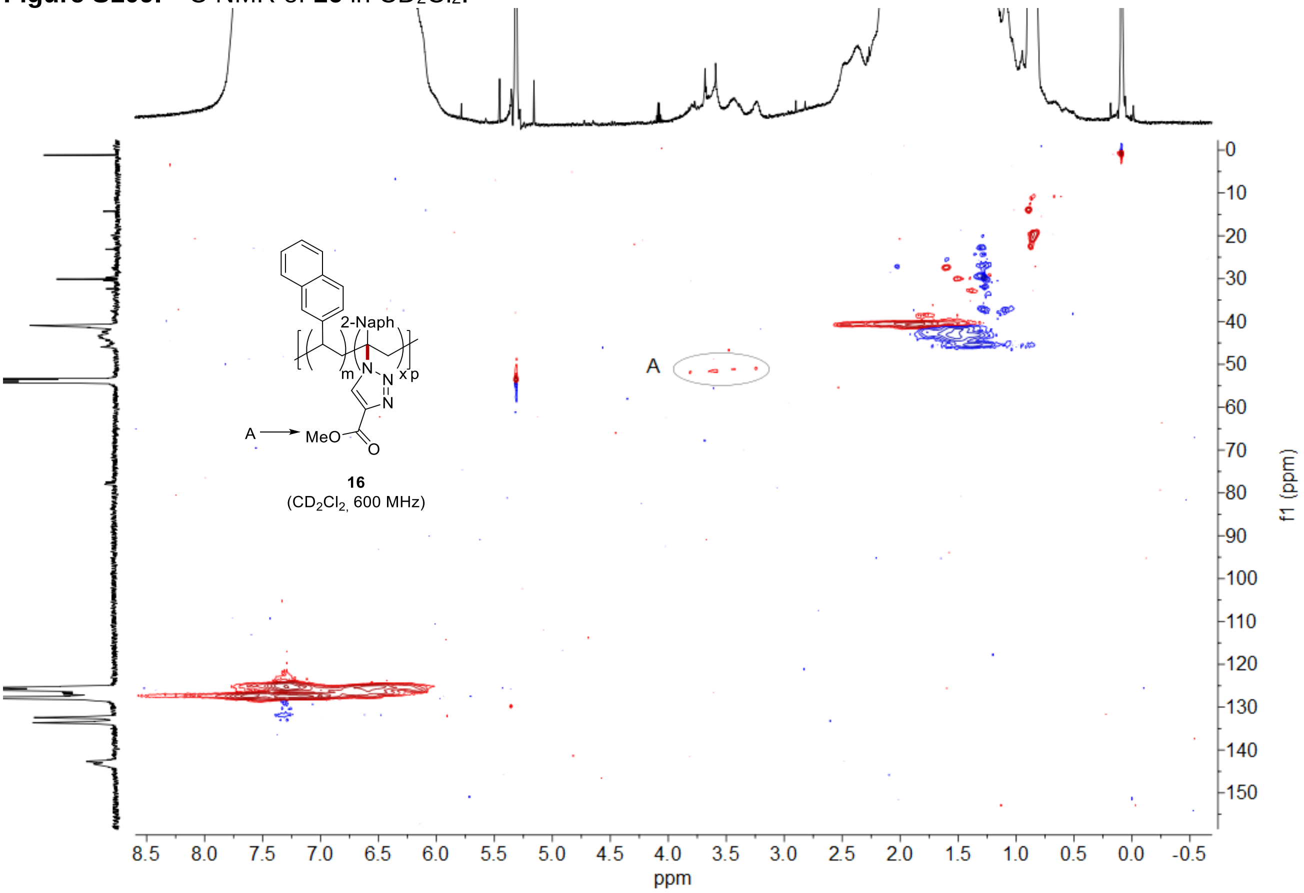


Figure S110. HSQC of **16** in CD$_2$Cl$_2$.

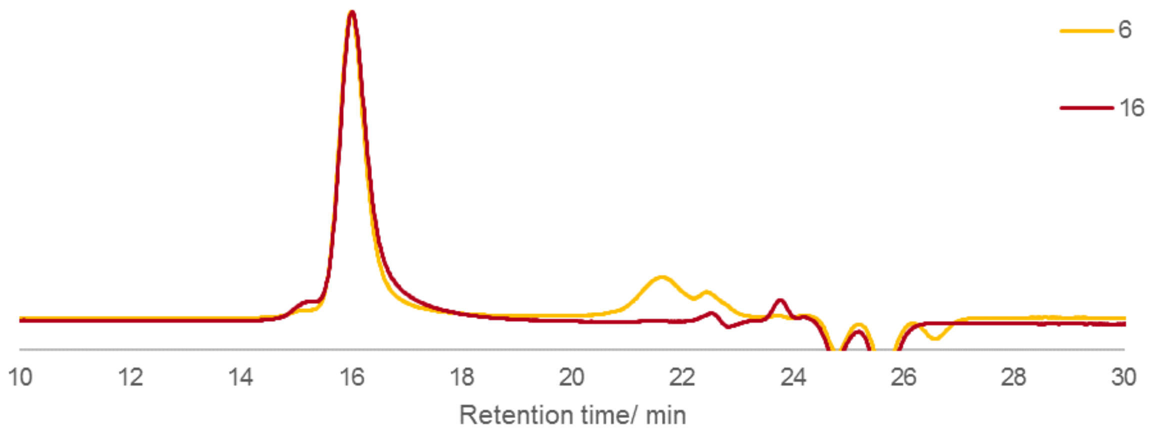


Figure S111. Normalized chromatogram of **6** (yellow) and modified polymer **16** (red).

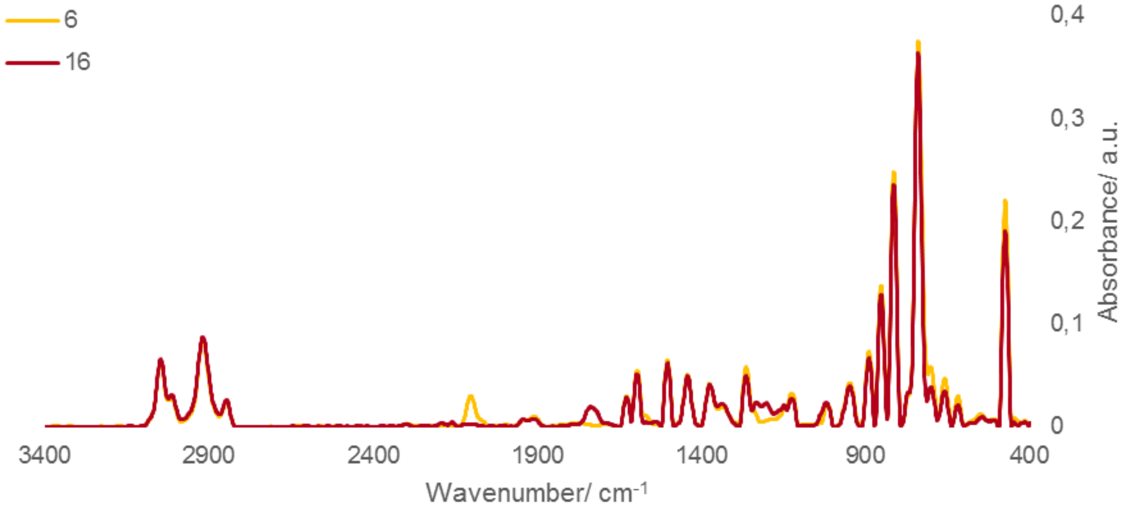


Figure S112. IR spectrum of azide polymer **6** (yellow) and 1,3-cycloaddition product **16** (red) in arbitrary units (a.u.).

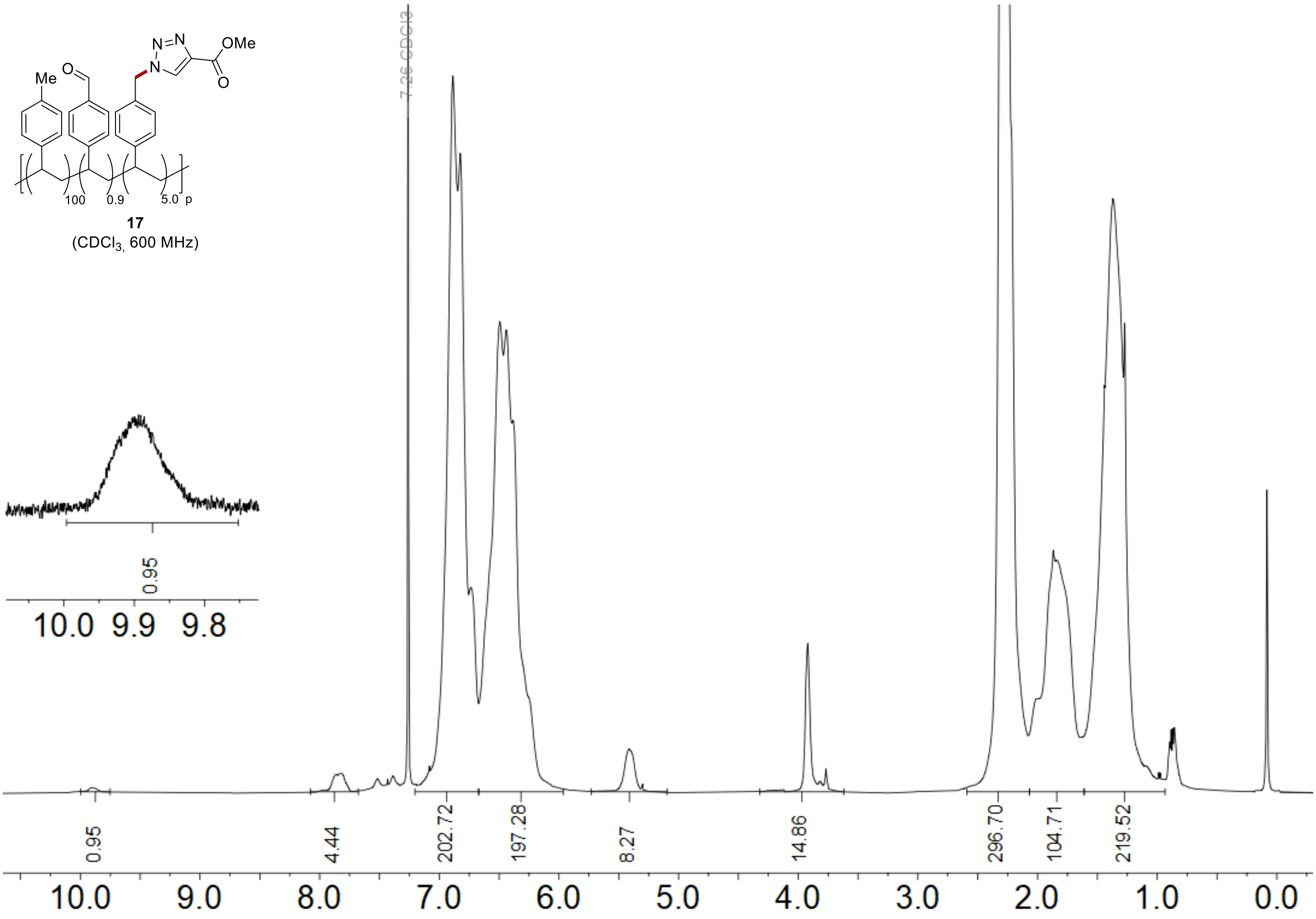


Figure S113. ^{1}H NMR of **17** in CDCl$_3$.

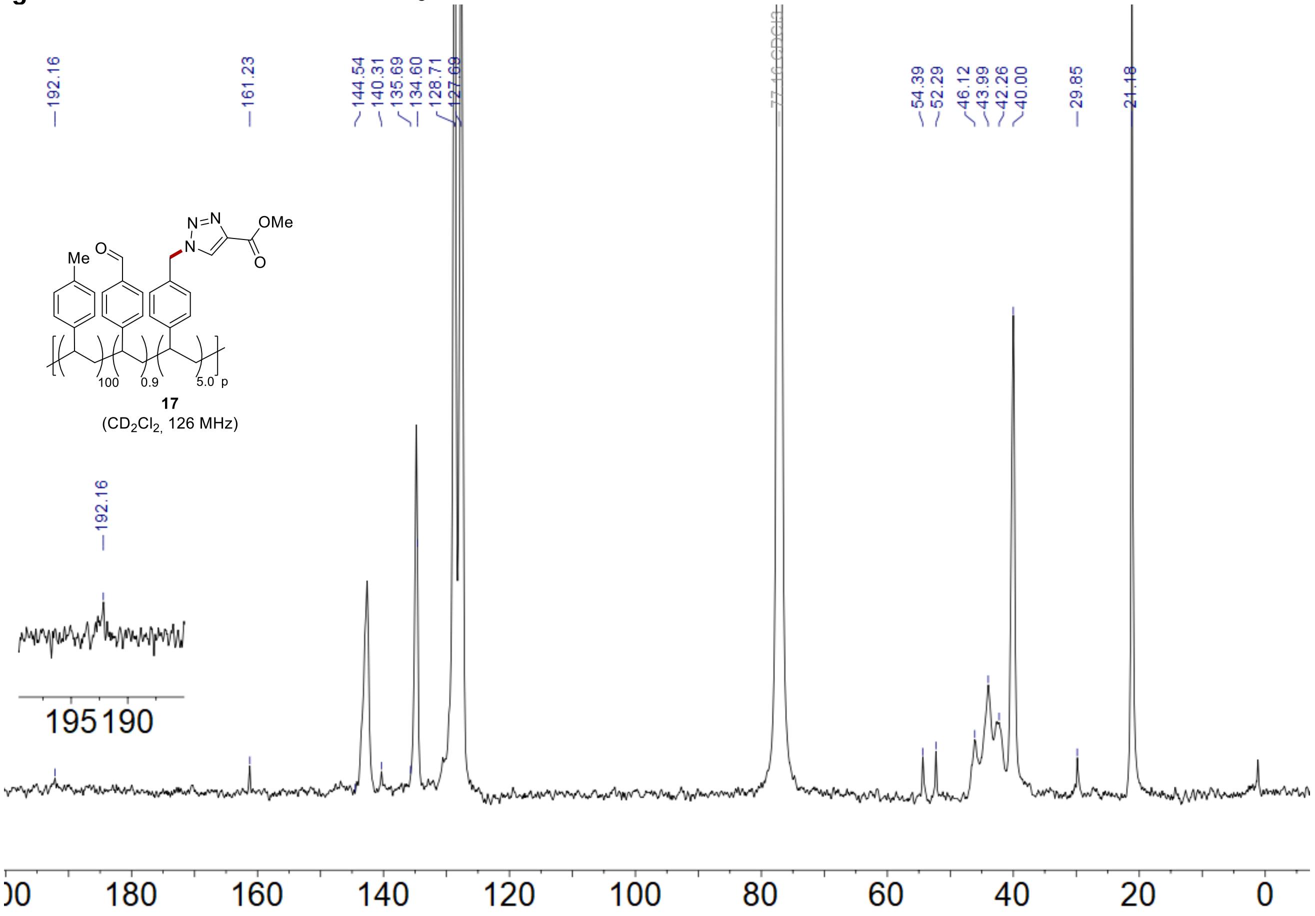


Figure S114. ^{13}C NMR of **17** in CDCl$_3$.

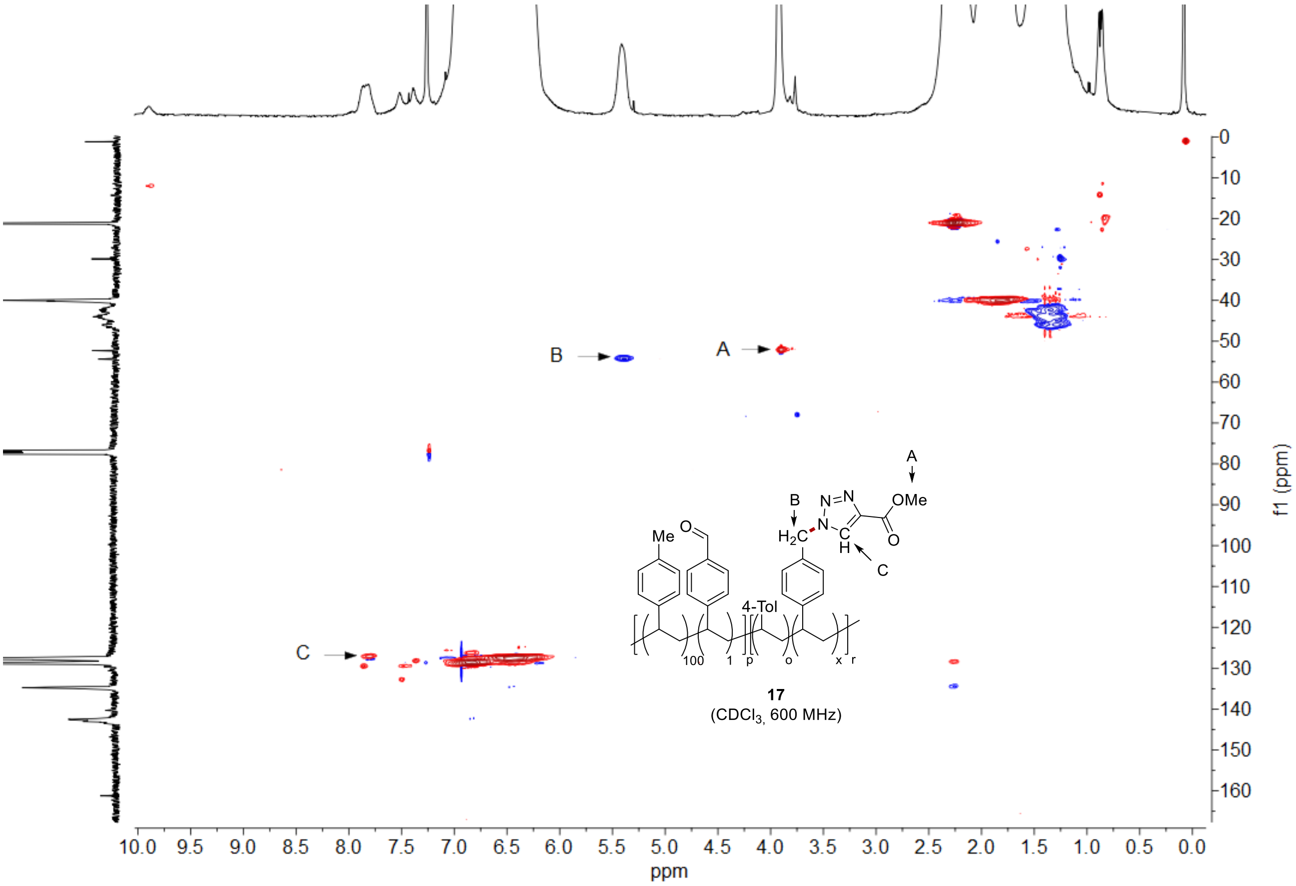


Figure S115. HSQC of **17** in CDCl3.

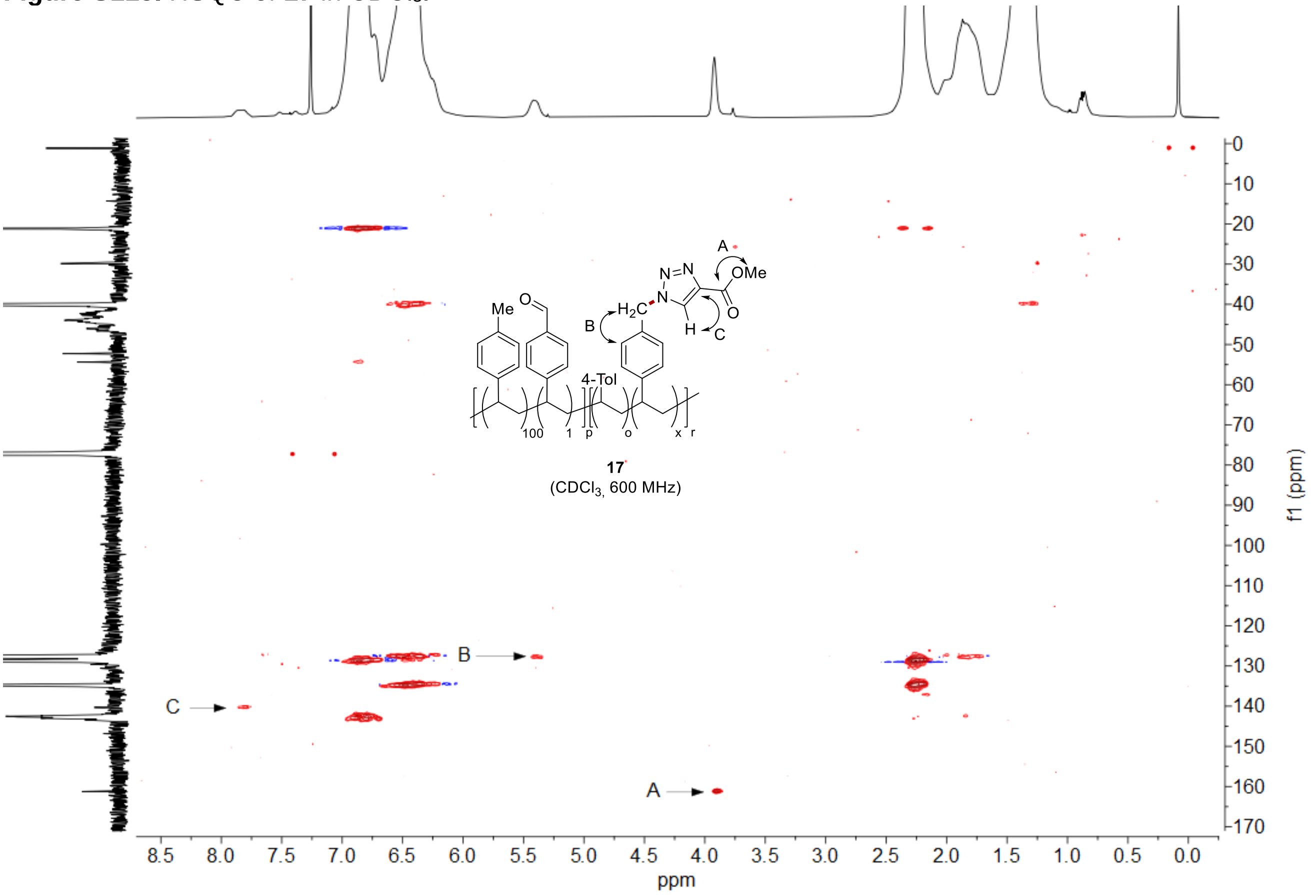


Figure S116. HMBC NMR of **17** in CDCl3.

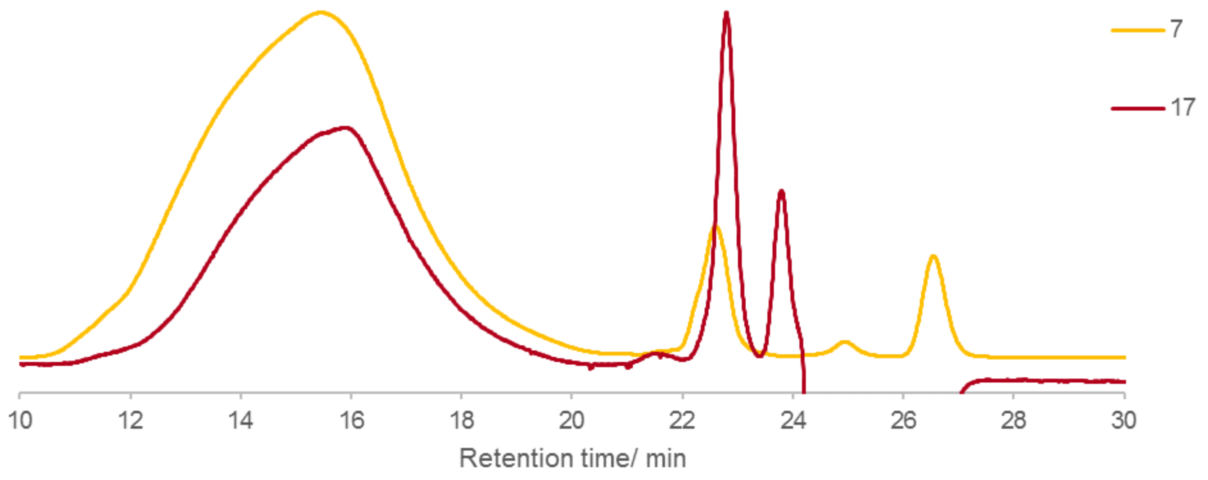


Figure S117. Normalized chromatogram of **7** (yellow) and modified polymer **17** (red).

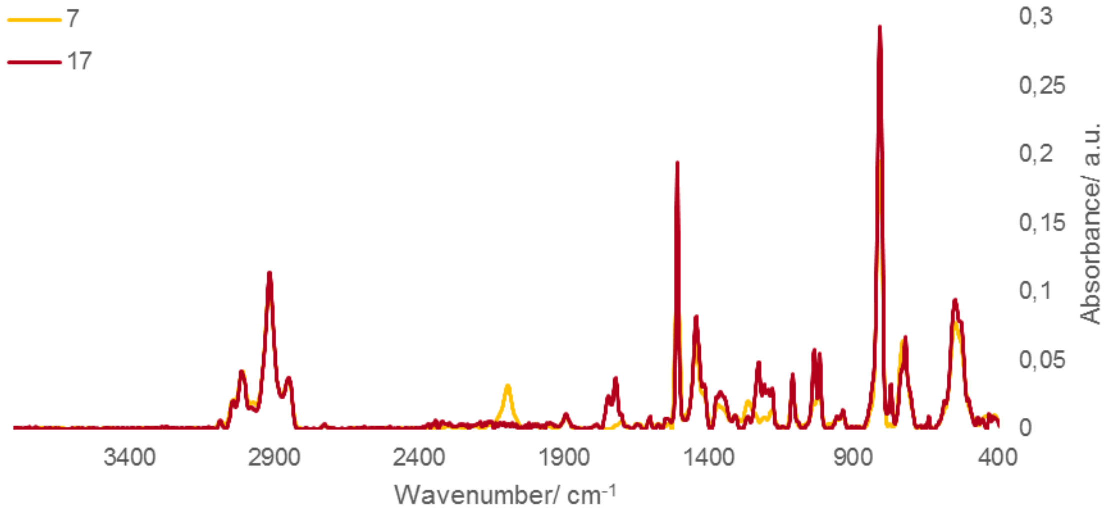


Figure S118. IR spectrum of azide polymer **7** (yellow) and 1,3-cycloaddition product **17** (red) in arbitrary units (a.u.).

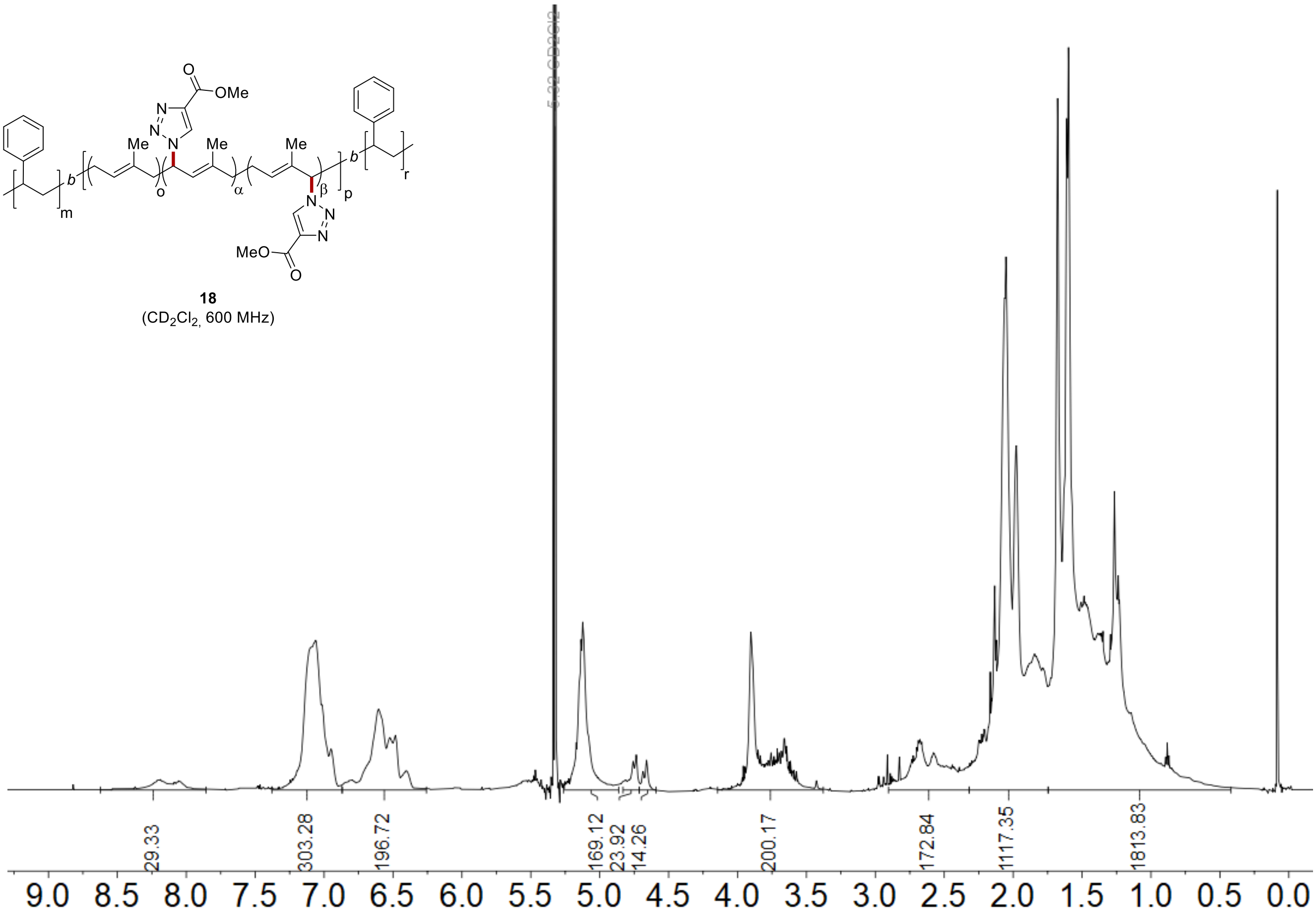


Figure S119. ^{1}H NMR of **18** in CD_2Cl_2.

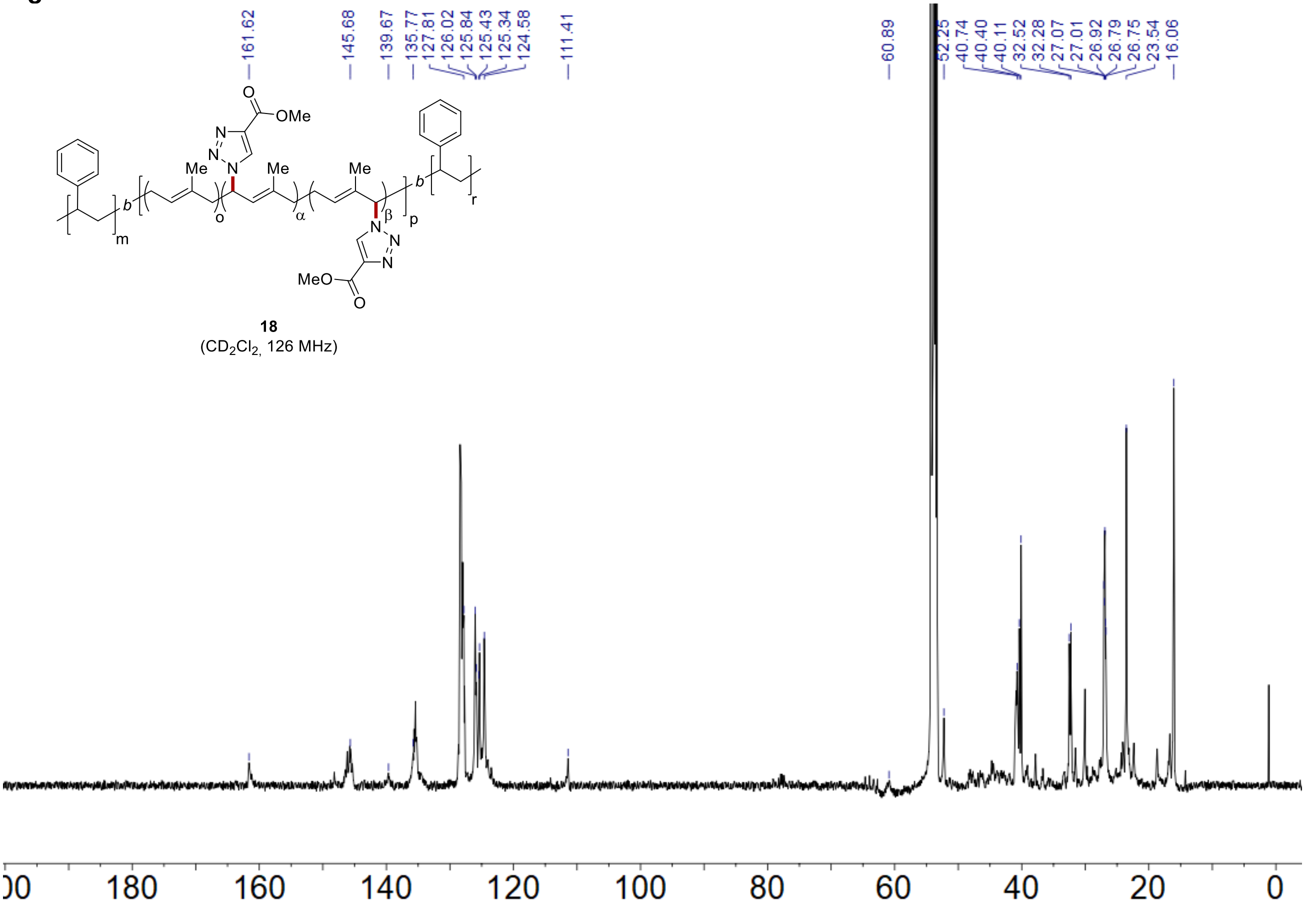


Figure S120. ^{13}C NMR of **18** in CD_2Cl_2.

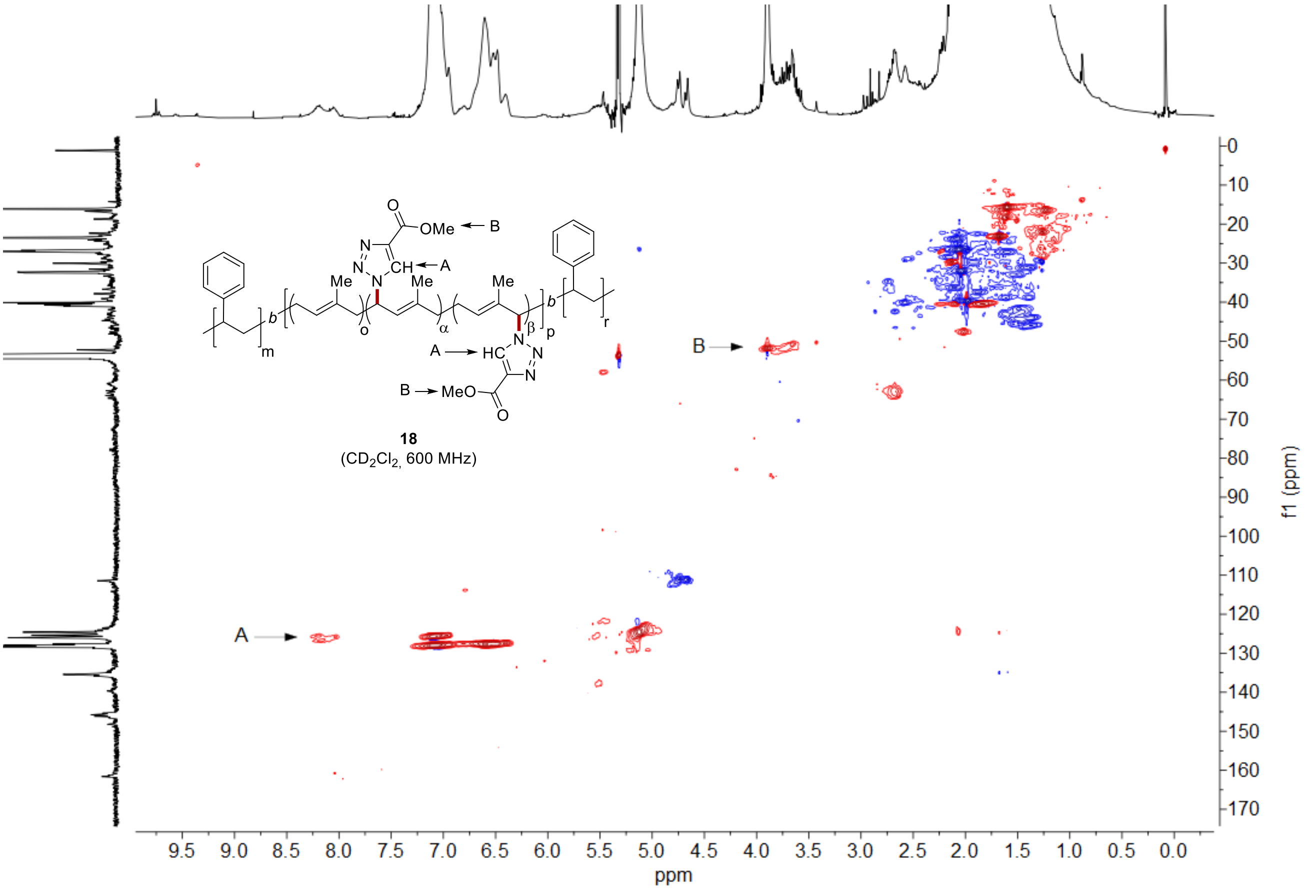


Figure S121. HSQC of **18** in CD$_2$Cl$_2$.

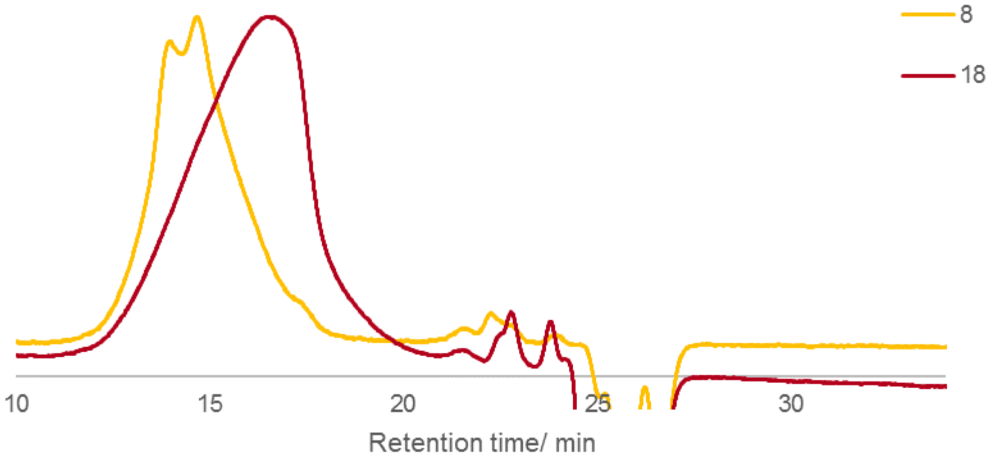


Figure S122. Normalized chromatogram of **8** (yellow) and modified polymer **18** (red).

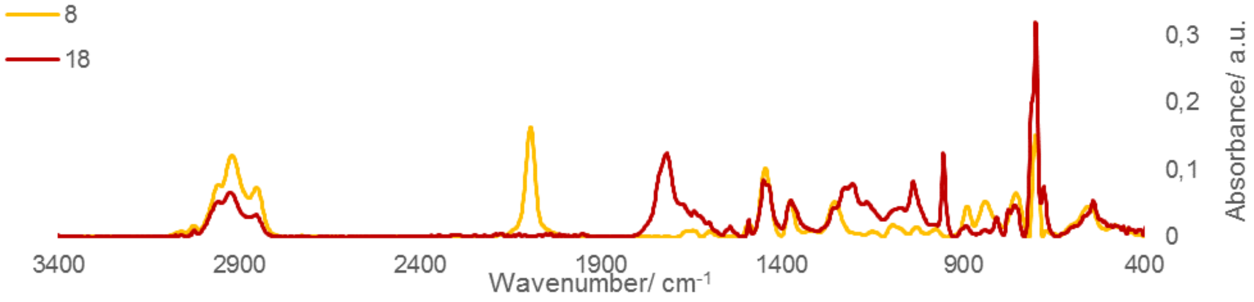


Figure S123. IR spectrum of azide polymer **8** (yellow) and 1,3-cycloaddition product **18** (red) in arbitrary units (a.u.).

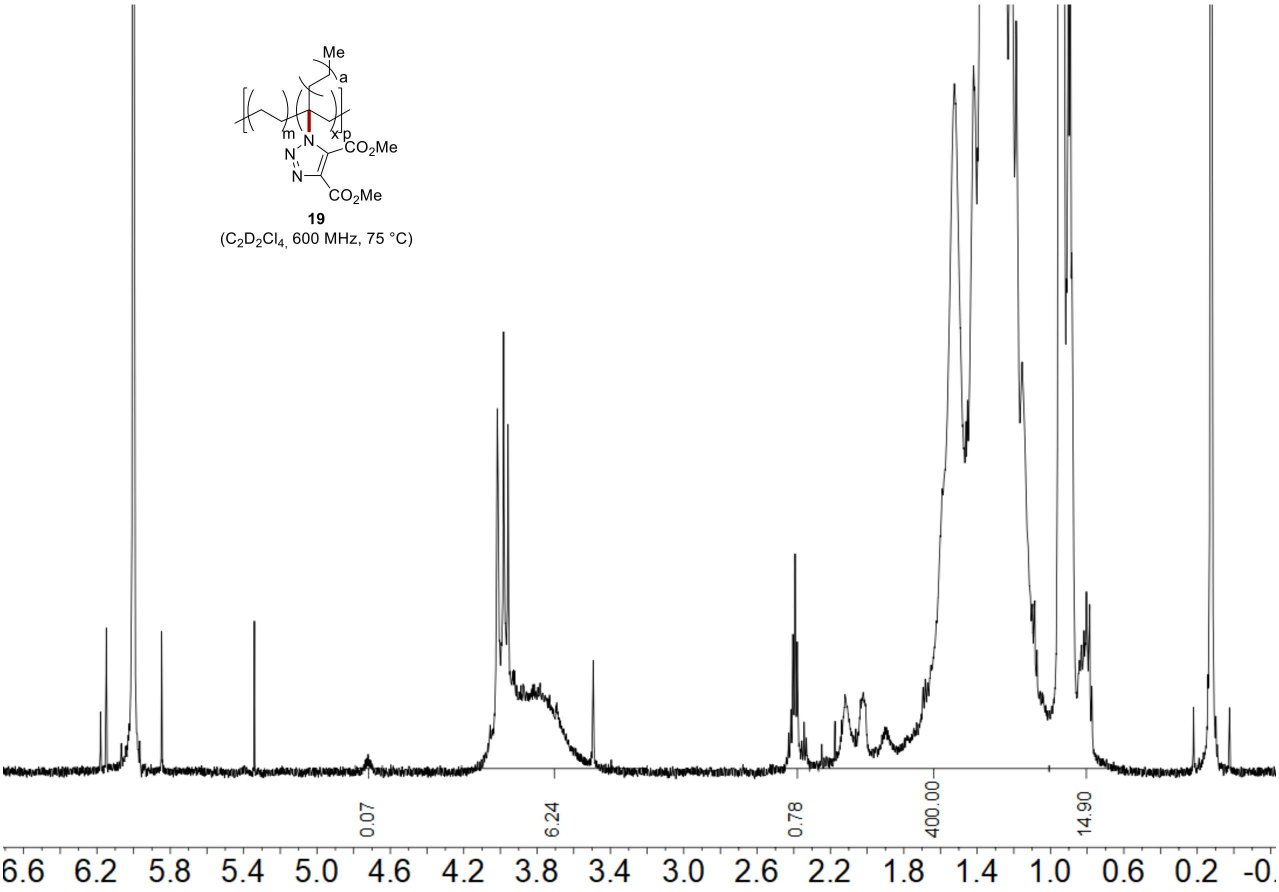


Figure S124. ^{1}H NMR of **19** in $C_2D_2Cl_4$ at 75 °C.

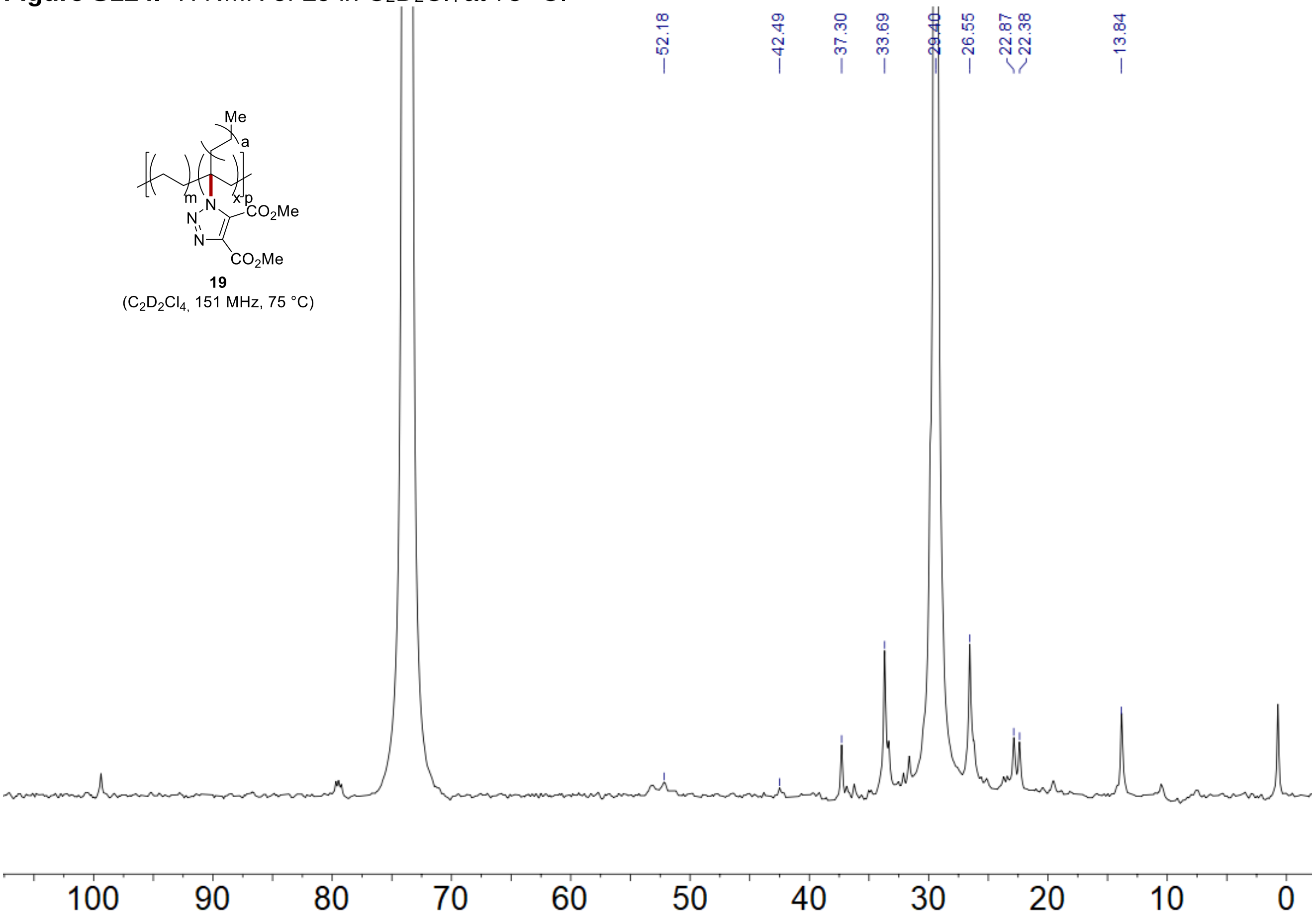


Figure S125. ^{13}C NMR of **19** in $C_2D_2Cl_4$ at 75 °C.

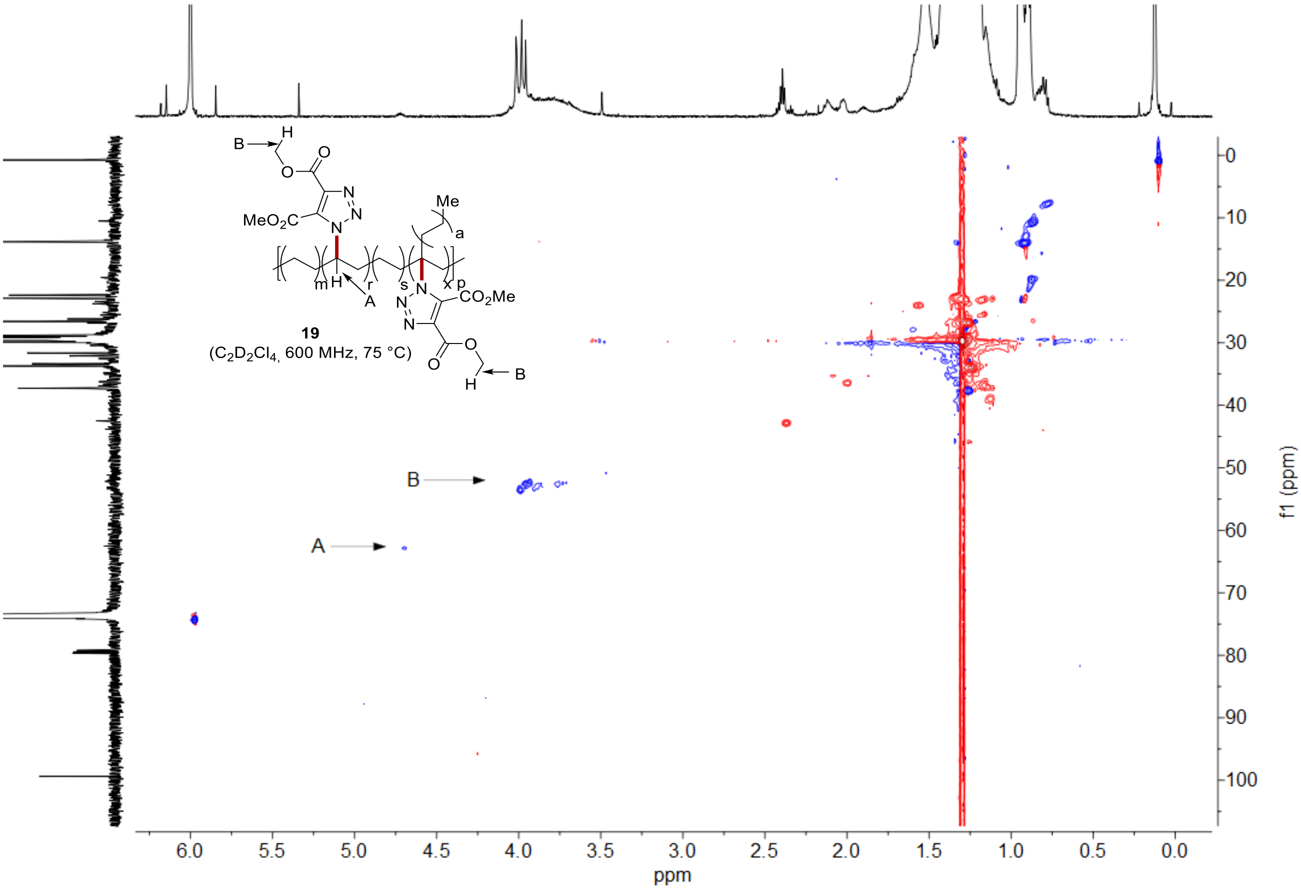


Figure S126. HSQC of **19** in $C_2D_2Cl_4$ at 75 °C.

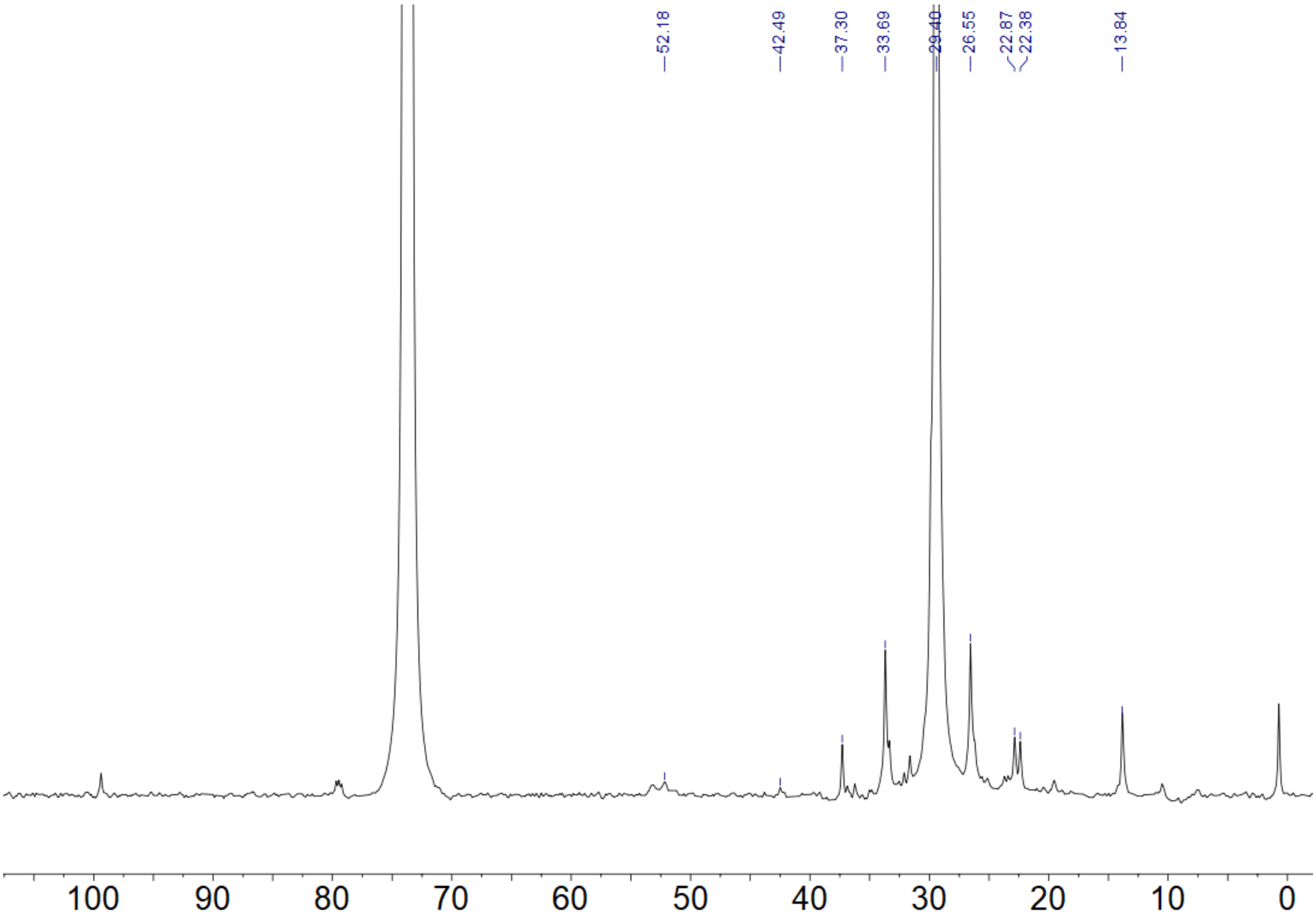


Figure S127. IR spectrum of azide polymer **9** (yellow) and 1,3-cycloaddition product **19** (red) in arbitrary units (a.u.).

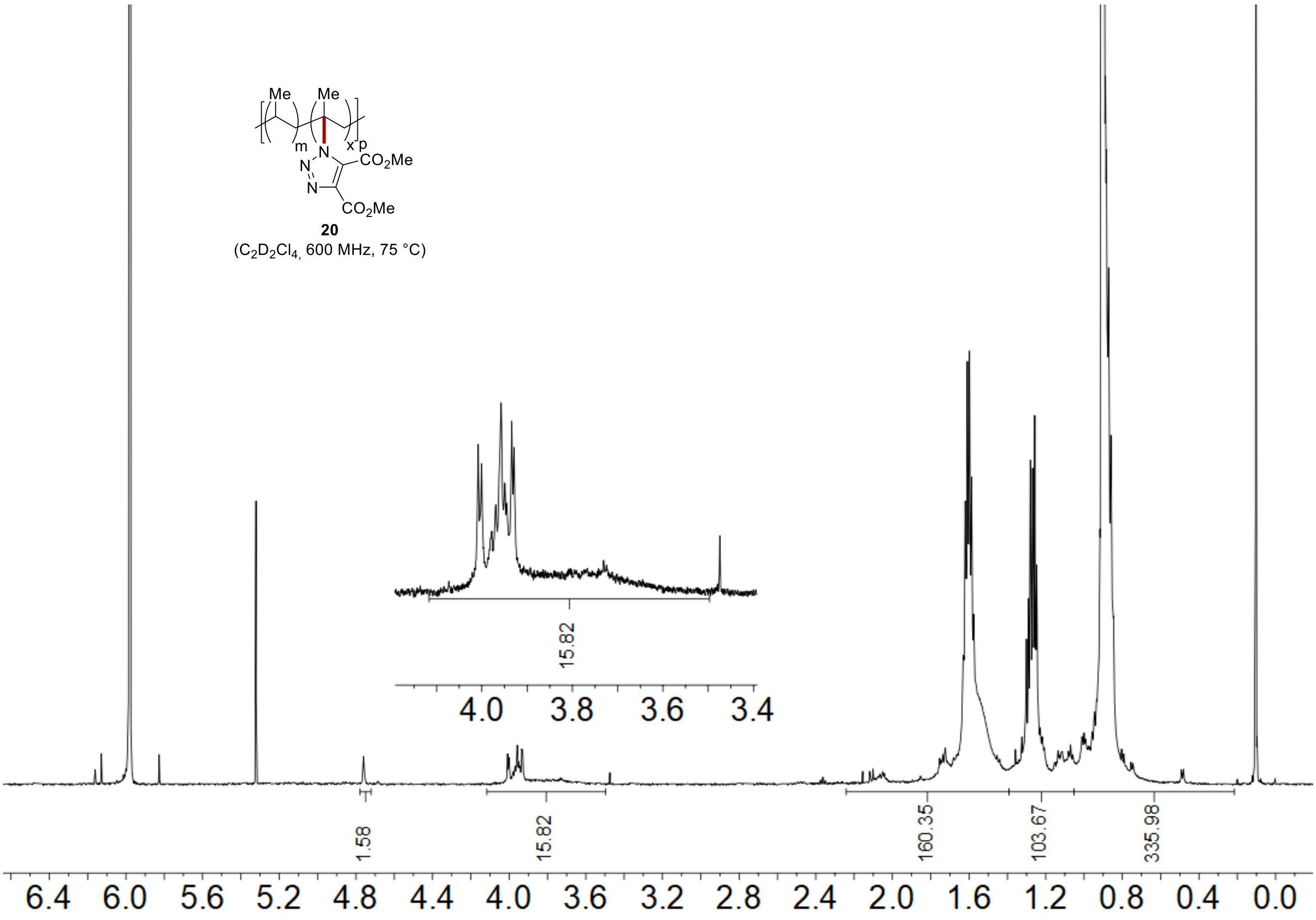


Figure S128. ^{1}H NMR of **20** in $C_2D_2Cl_4$ at 75 °C.

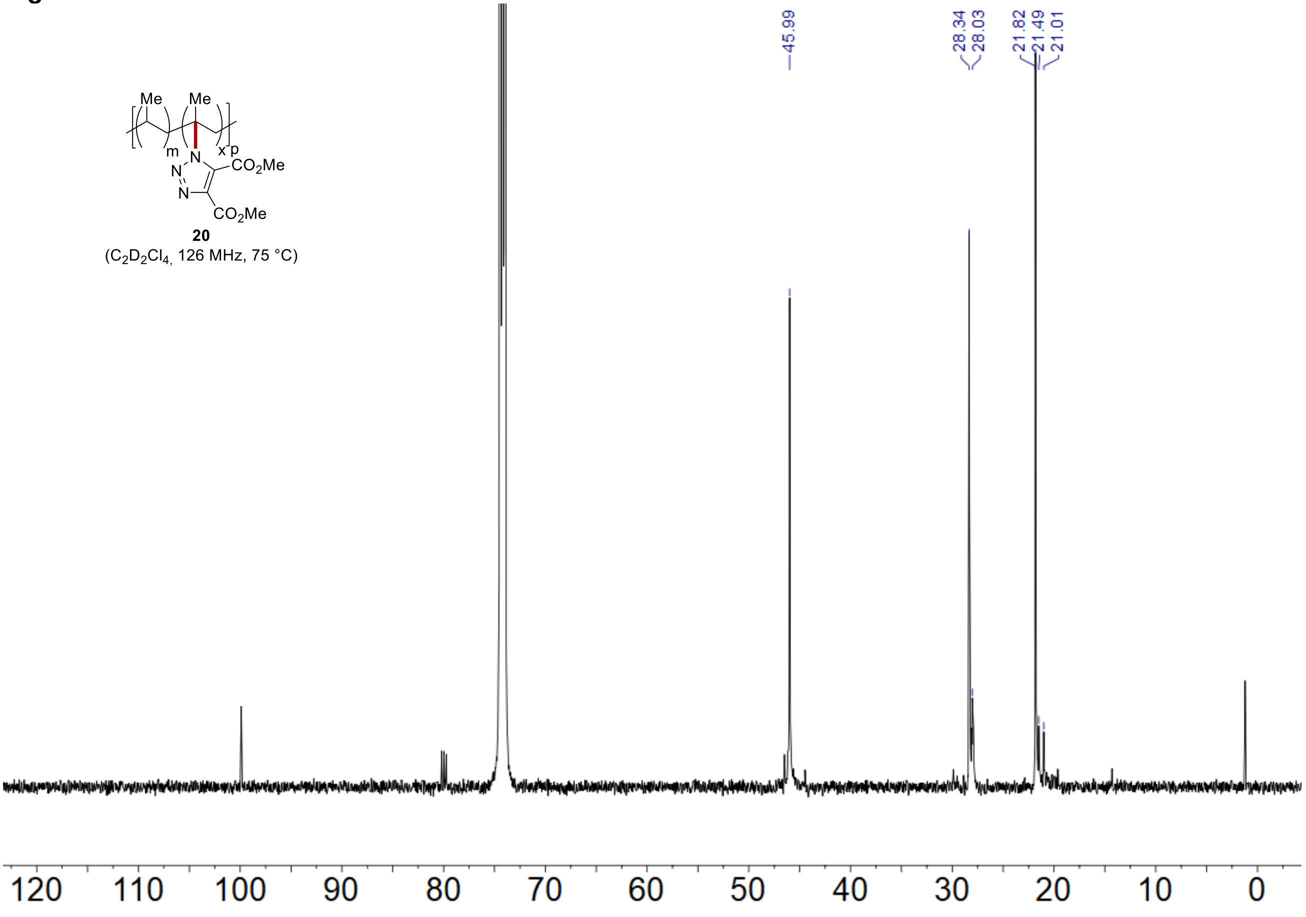


Figure S129. ^{13}C NMR of **20** in $C_2D_2Cl_4$ at 75 °C.

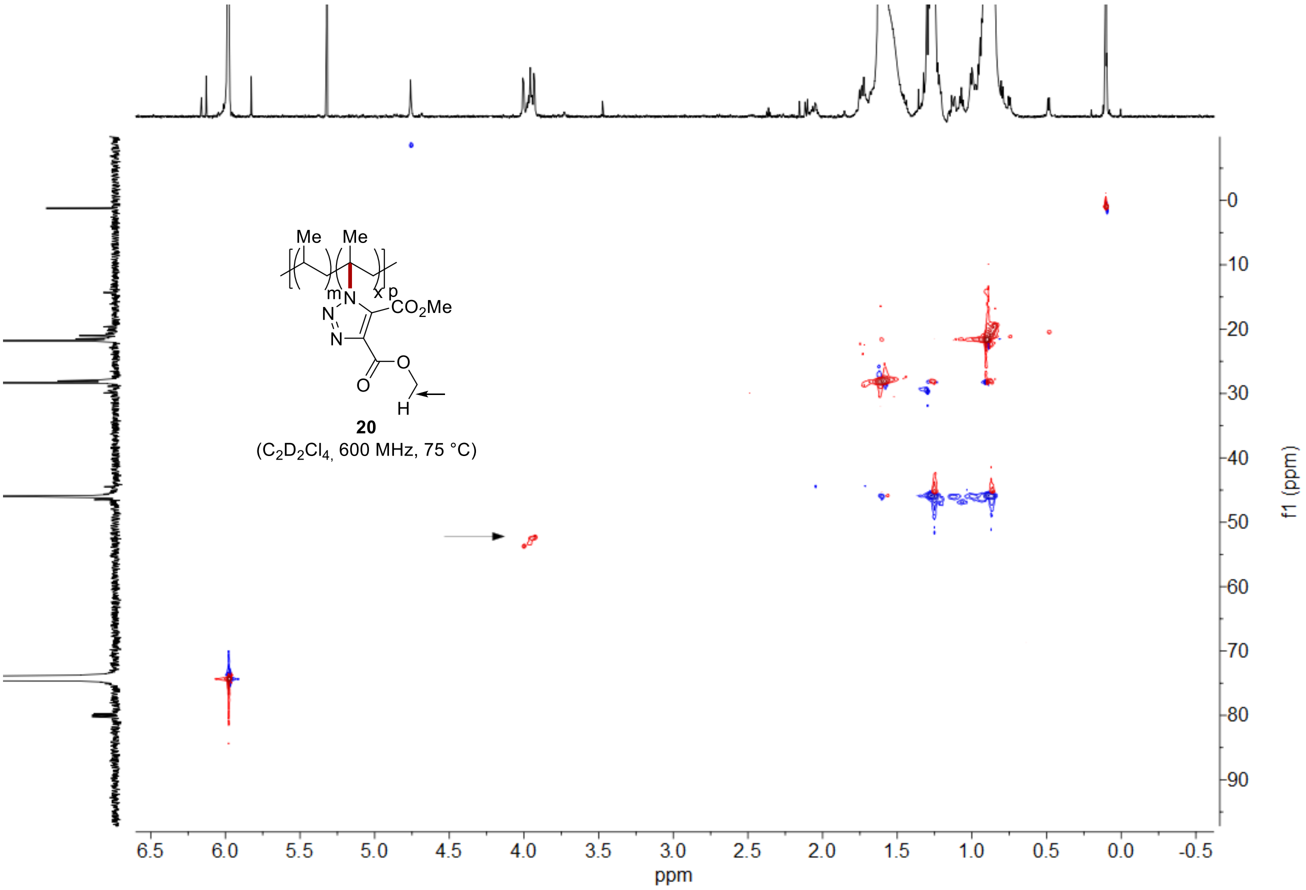


Figure S130. HSQC of **20** in $C_2D_2Cl_4$ at 75 °C.

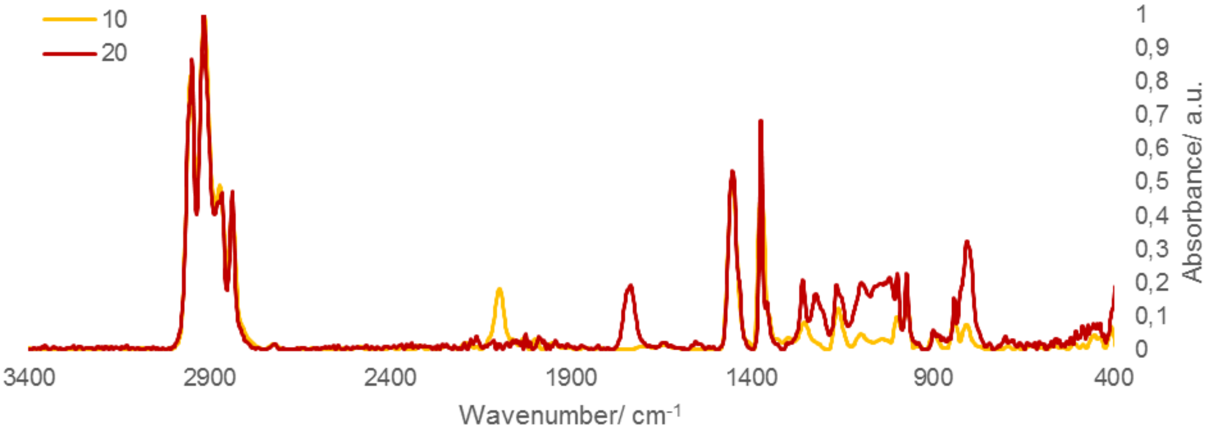


Figure S131. IR spectrum of azide polymer **10** (yellow) and 1,3-cycloaddition product **20** (red) in arbitrary units (a.u.).

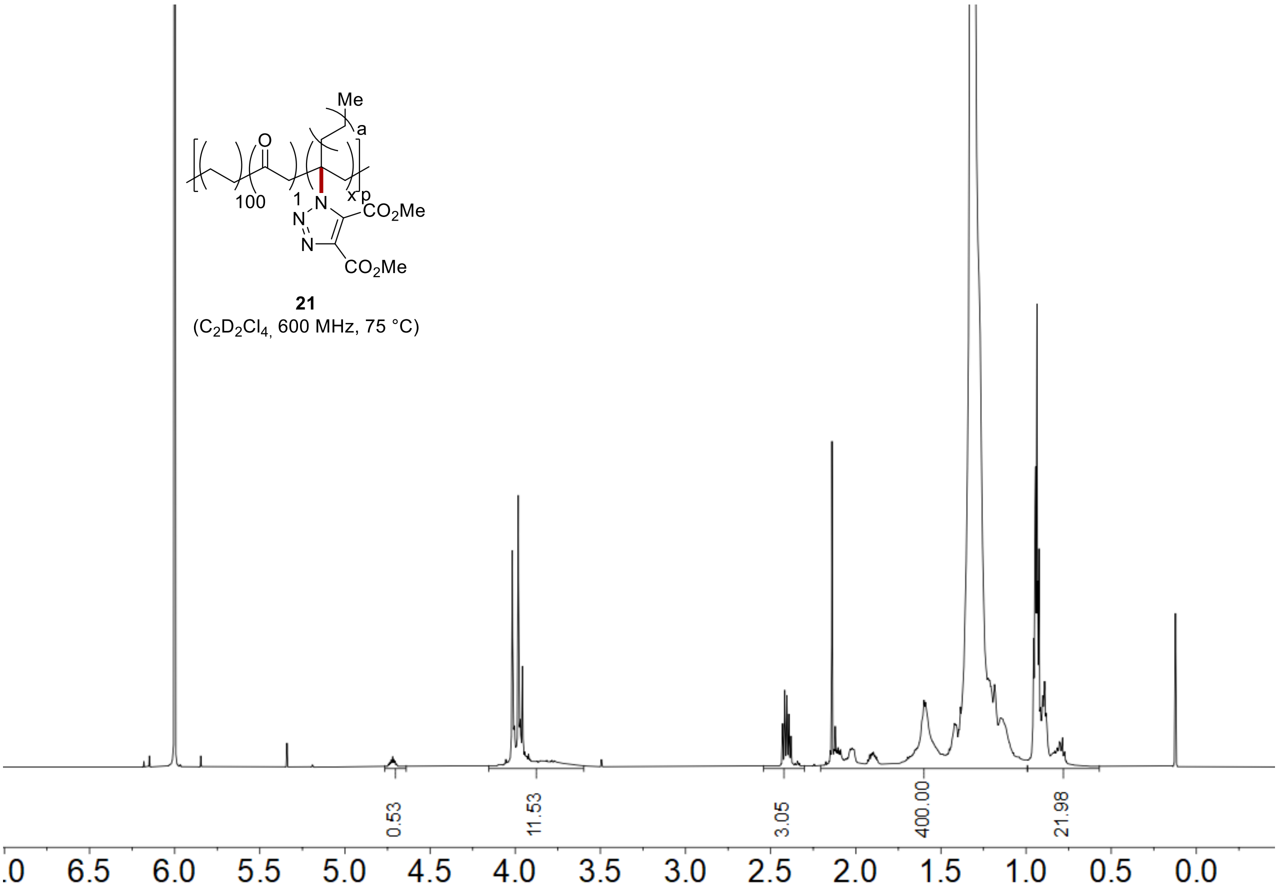


Figure S132. ^{1}H NMR of **21** in $C_2D_2Cl_4$ at 75 °C.

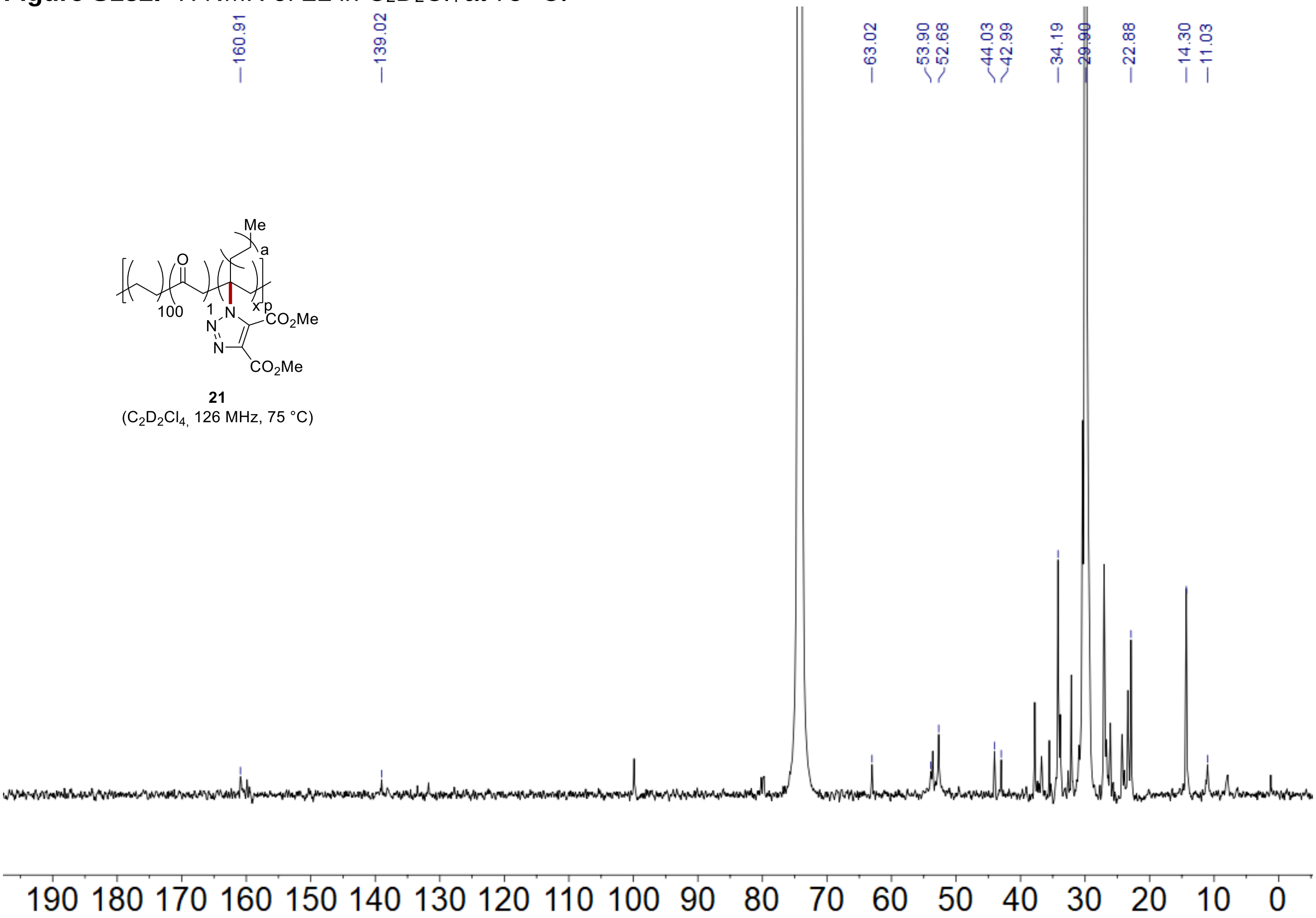


Figure S133. ^{13}C NMR of **21** in $C_2D_2Cl_4$ at 75 °C.

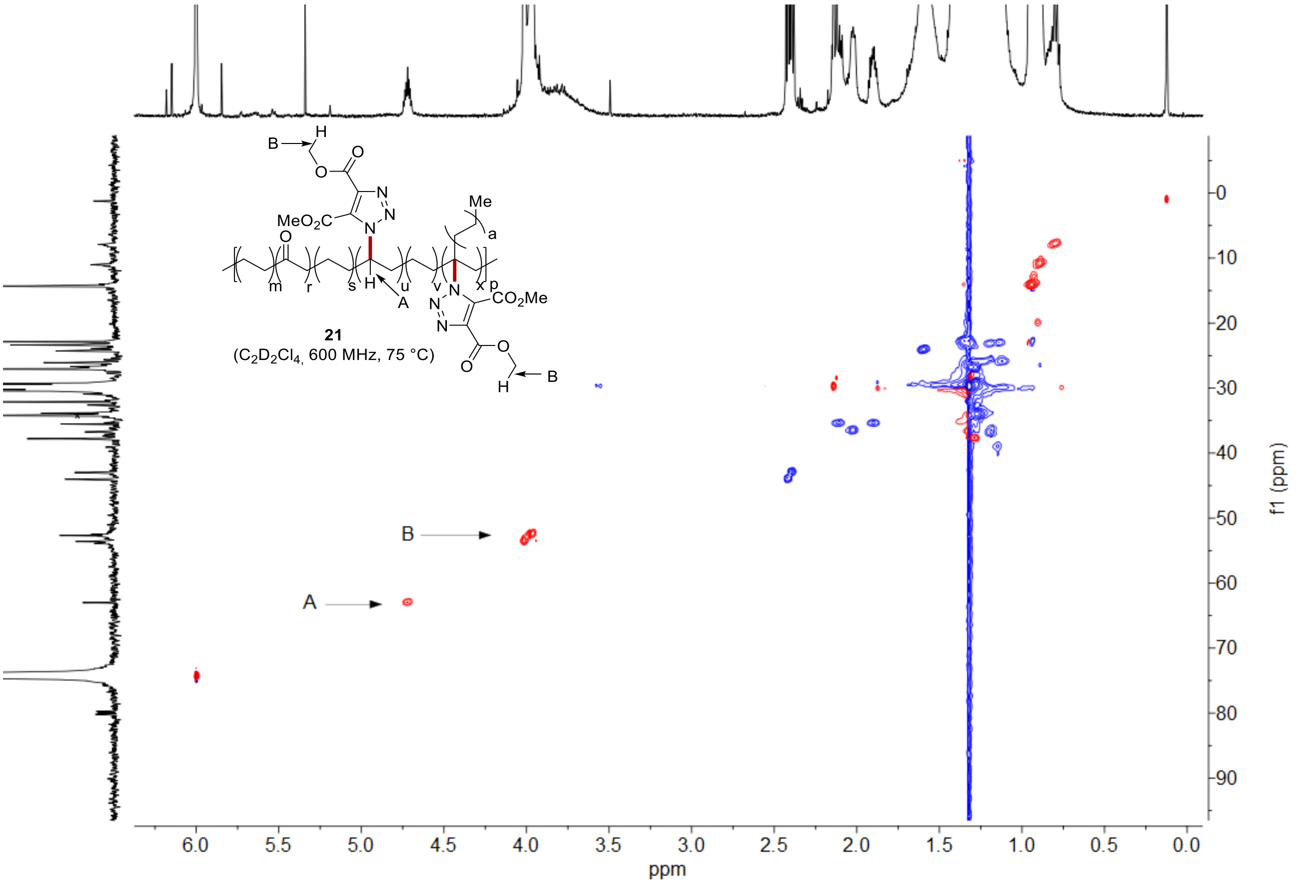


Figure S134. HSQC of **21** in $C_2D_2Cl_4$ at 75 °C.

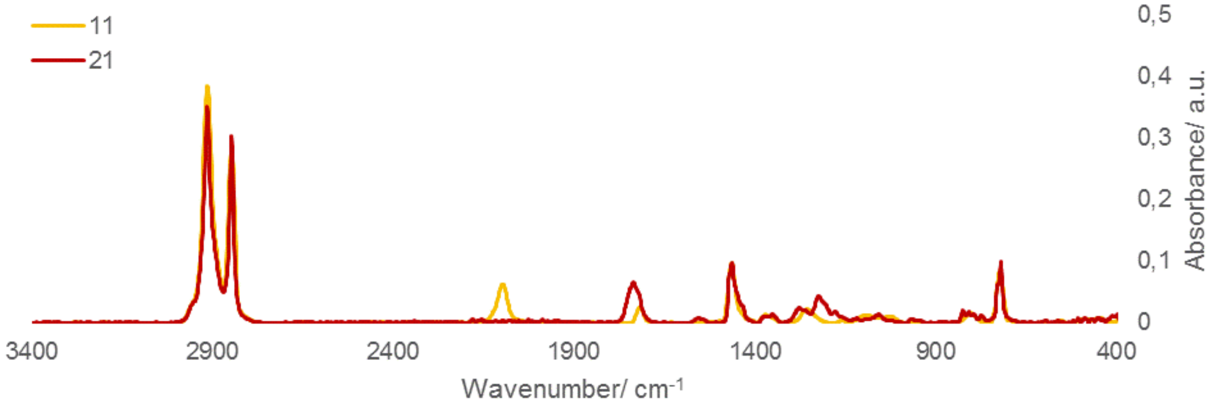


Figure S135. IR spectrum of azide polymer **11** (yellow) and 1,3-cycloaddition product **21** (red) in arbitrary units (a.u.).

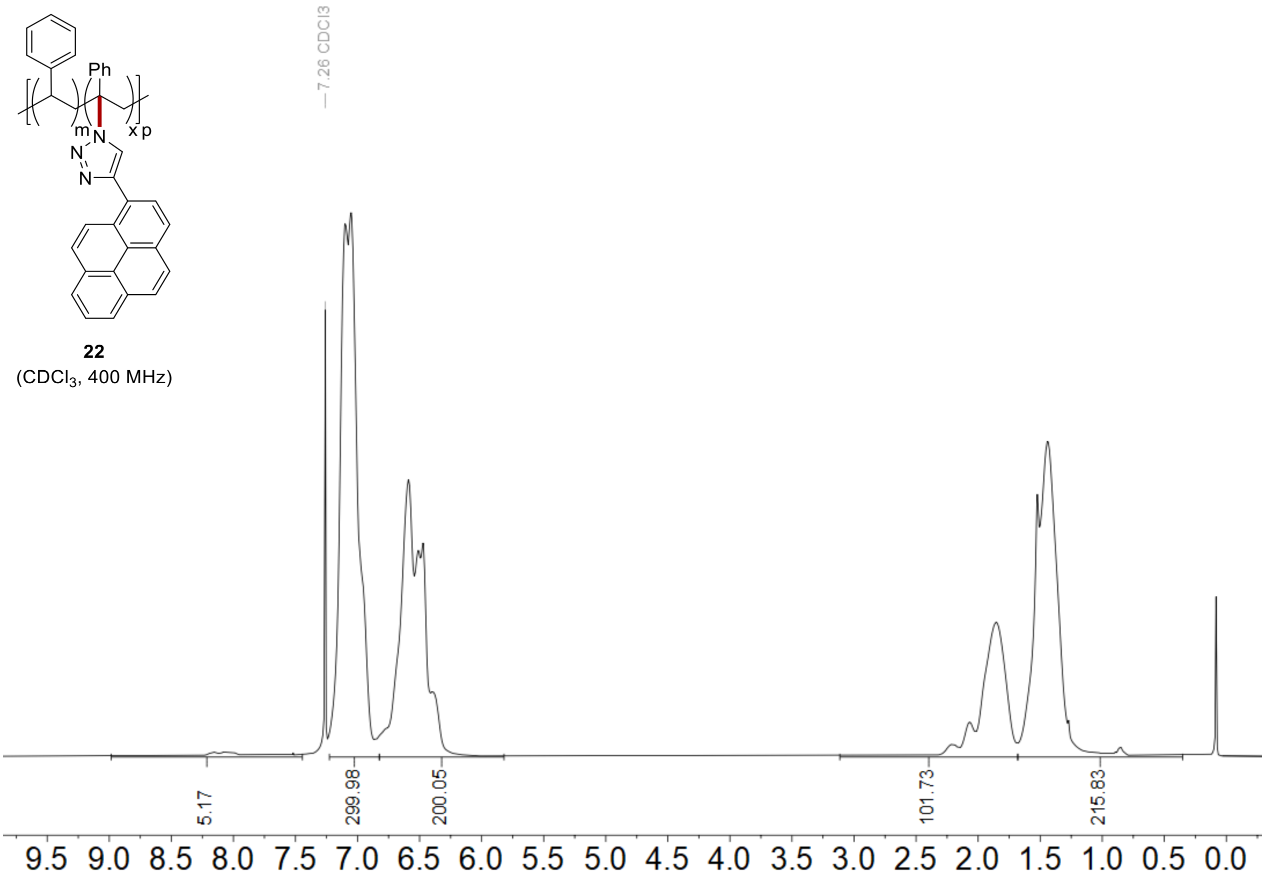


Figure S136. ^{1}H NMR of **22** in CDCl$_3$.

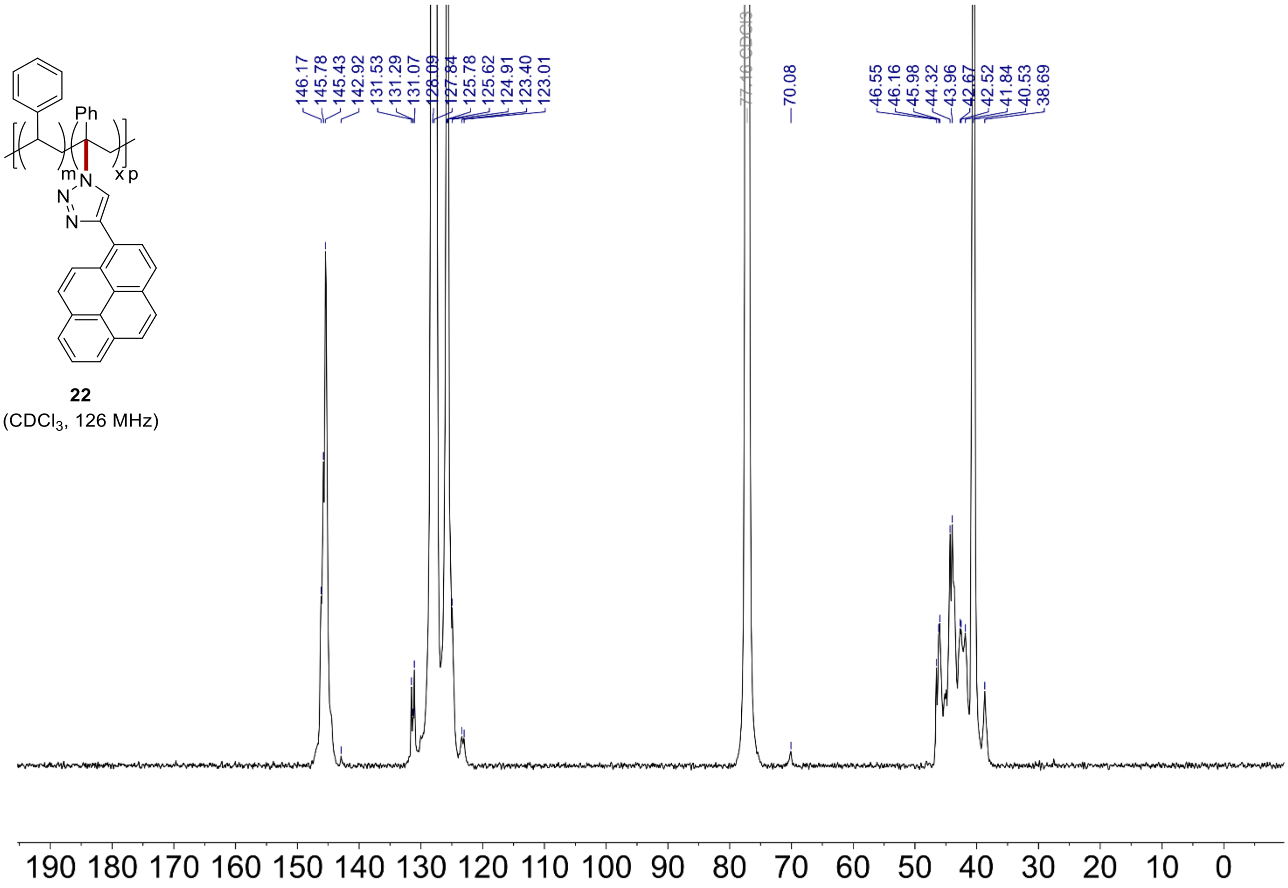


Figure S137. ^{13}C NMR of **22** in CDCl$_3$. Due to low azide functionalization of the parent polymer **12** (0.8 mol %), a sample of **22** with 3.8 mol % functionalization was used to record the ^{13}C NMR spectrum.

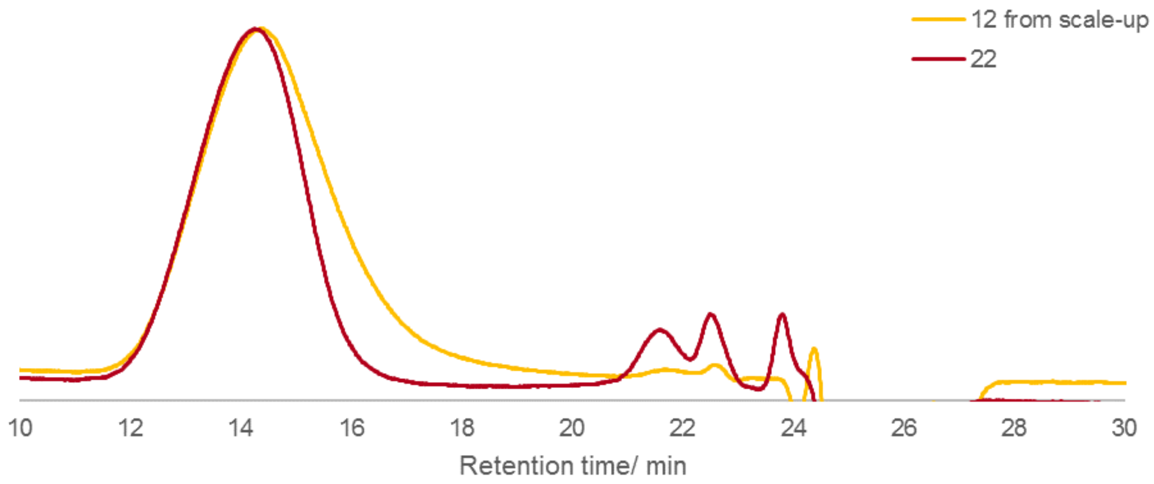


Figure S138. Normalized chromatogram of **12** (yellow) and modified polymer **22** (red) using RI-detection.

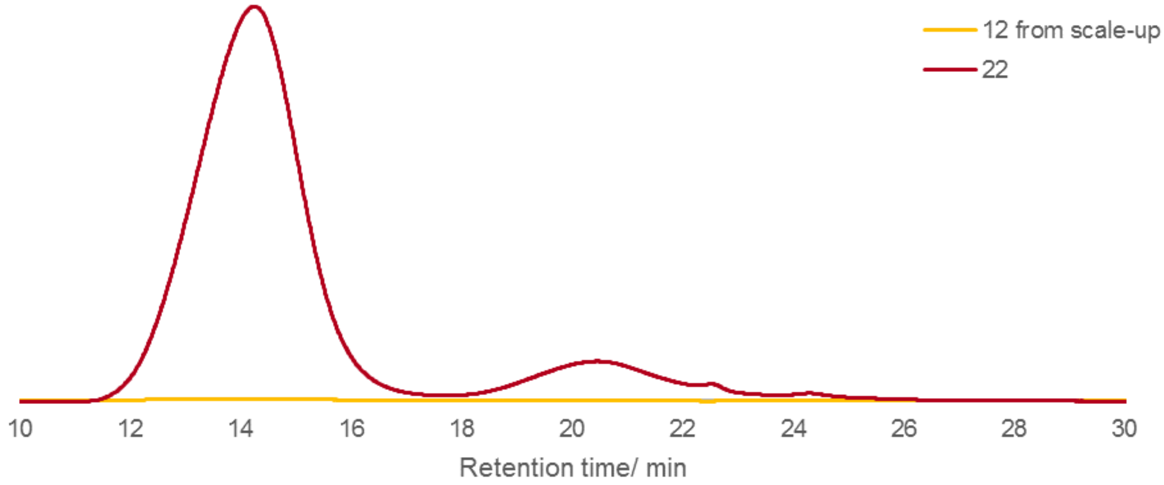


Figure S139. Chromatogram of **12** (yellow) and modified polymer **22** (red) using UV-detection at 350 nm in arabitary unites (a.u.). The detection of the molecular weight distribution at 350 nm indicates the successful appendance of the pyrene moiety to the polymer chains.

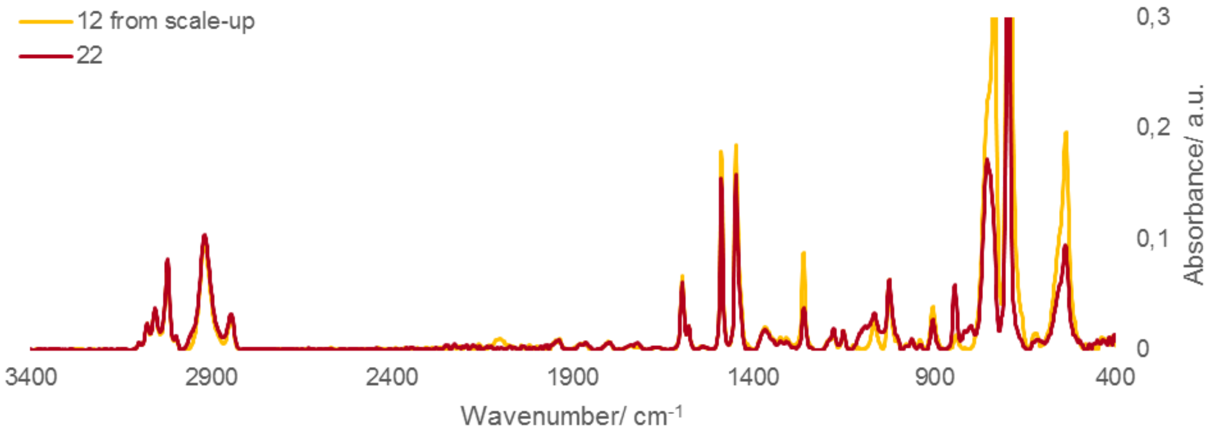


Figure S140. IR spectrum of **12** (yellow) and modified polymer **22** (red) in arbitrary units (a.u.).

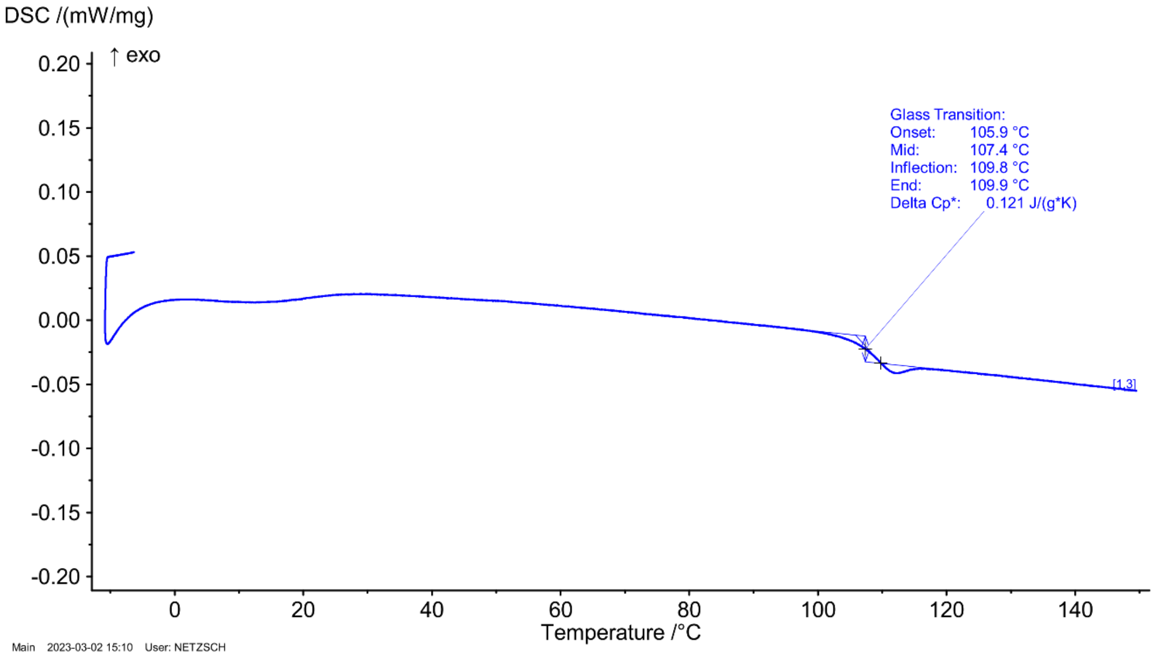


Figure S141. DSC of **22**.

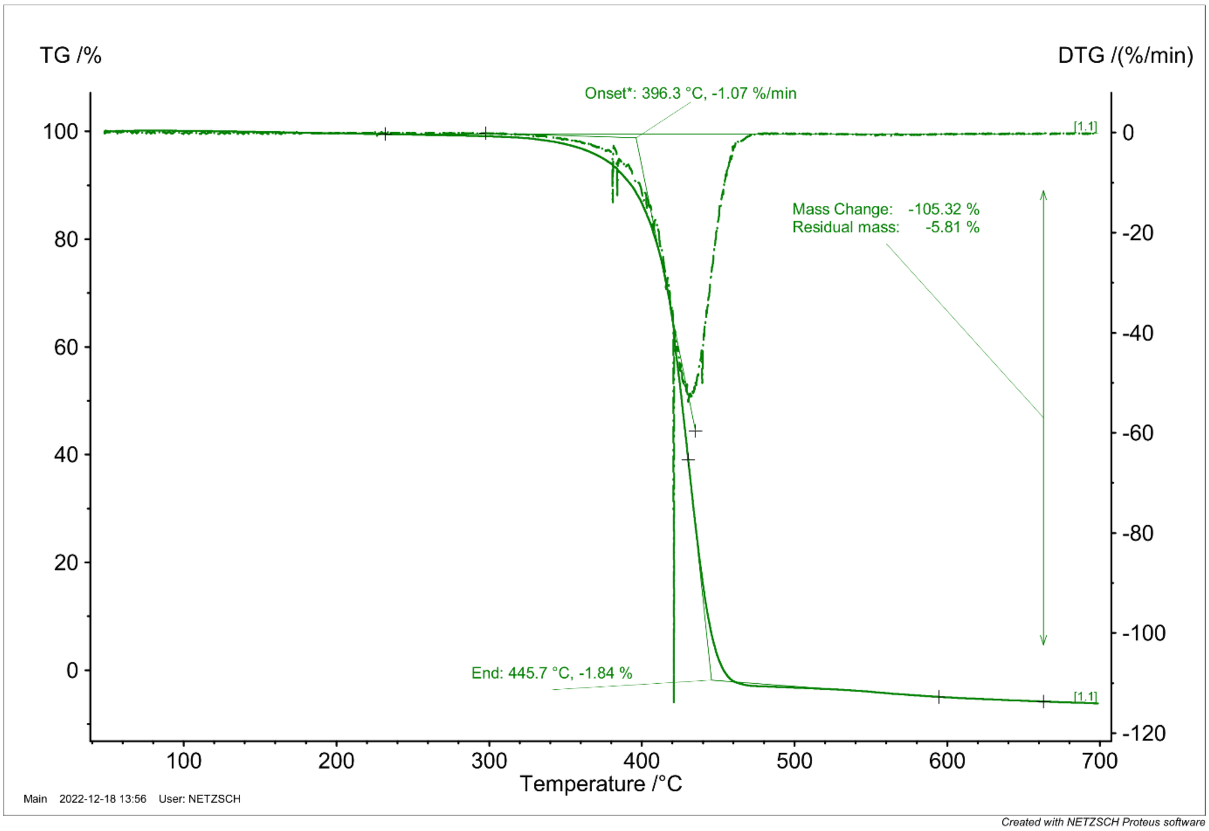


Figure S142. TGA of **22**.

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