Electronic Supplementary Material (ESI) for RSC Sustainability.

Supporting Information

Complete depolymerization of poly(ester-*alt*-thioether)s under mild conditions into AB functional monomers

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Table S1 : Experimental conditions and molecular characteristics of the polymers obtained by the copolymerization of NHTL with various epoxides in THF (1.8 mol/L) at 50°C using benzyl alcohol and BEMP base as initiating system and [OH]:[BEMP]:[NHTL]:[Epoxide] ratio equal to 1:1:25:25.

Run	Epoxide	Time (h)	Cv[a] (%)	$M_{n,th}$ (g/mol)	$M_{n,RMN}$[b] (g/mol)	$M_{n,SEC}$ (g/mol)	$M_{w,SEC}$ (g/mol)	$Đ$
A1	BO	6.5	100	5890	6800	4380	5650	1.30
A2	BO	7	100	5890	7360	4690	6050	1.29
A3	BO	60	38	2300	3200	1710	2090	1.22
A4	BO	7	100	5890	6100	3357	5300	1.58
A5	BO	7	100	5890	8200	2900	3900	1.34
A6	*t*BuGE	6	100	7360	8200	5200	6920	1.34
A7	*t*BuGE	6	100	7360	7360	4680	6470	1.38
A8	*t*BuGE	48	43	3220	1740	1770	2160	1.22
A9*	*t*BuGE	3	100	7360	6760	3330	8470	2.54

*: bulk polymerization

a: monomer conversion calculated by 1H NMR spectroscopy of the reaction medium by comparison of the free monomer signal integration with the corresponding polymer chain signal integration

b: experimental molar mass determined by 1H NMR spectroscopy of the purified product by comparison of a initiator signal integration with a polymer chain signal integration

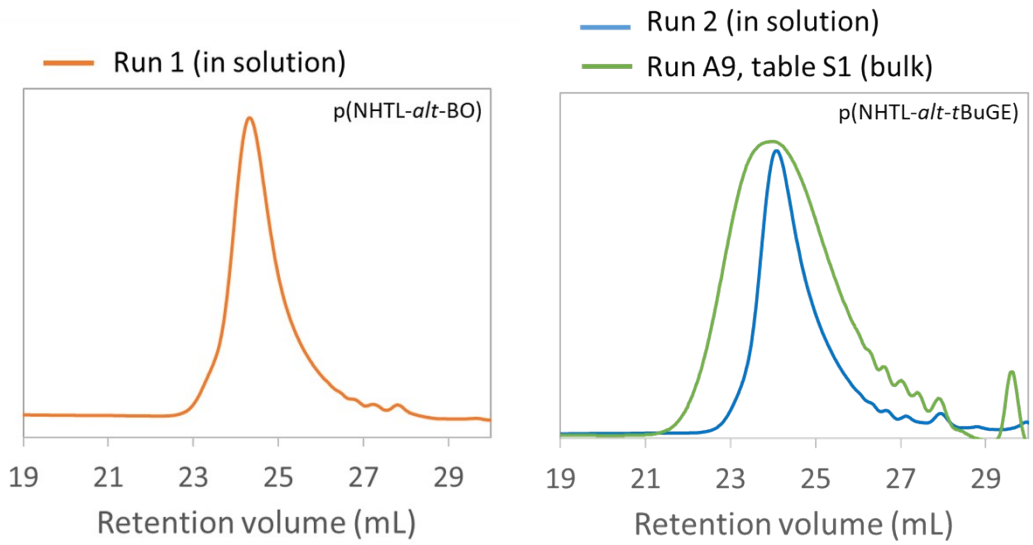


Figure S1: SEC analysis of p(NHTL-*alt*-BO) on the right (run 1, table 1 in orange) and p(NHTL-*alt*-*t*BuGE) on the left (run 2, table 1 in blue and run A9, table S1 in green) in THF at 40°C.

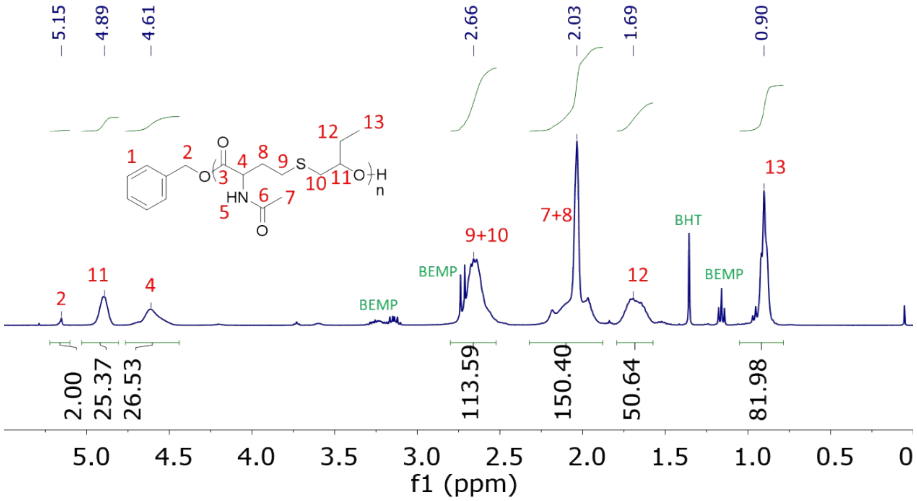


Figure S2: ^{1}H NMR spectrum of p(NHTL-*alt*-BO) (run 1, table 1) in $CDCl_3$ at 25°C.

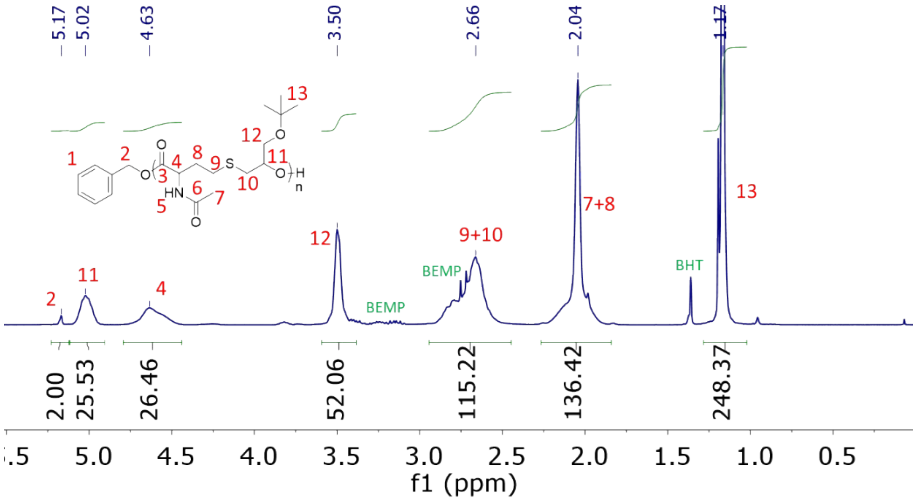


Figure S3: ^{1}H NMR spectrum of p(NHTL-*alt*-*t*BuGE) (run 2, table 1) in $CDCl_3$ at 25°C.

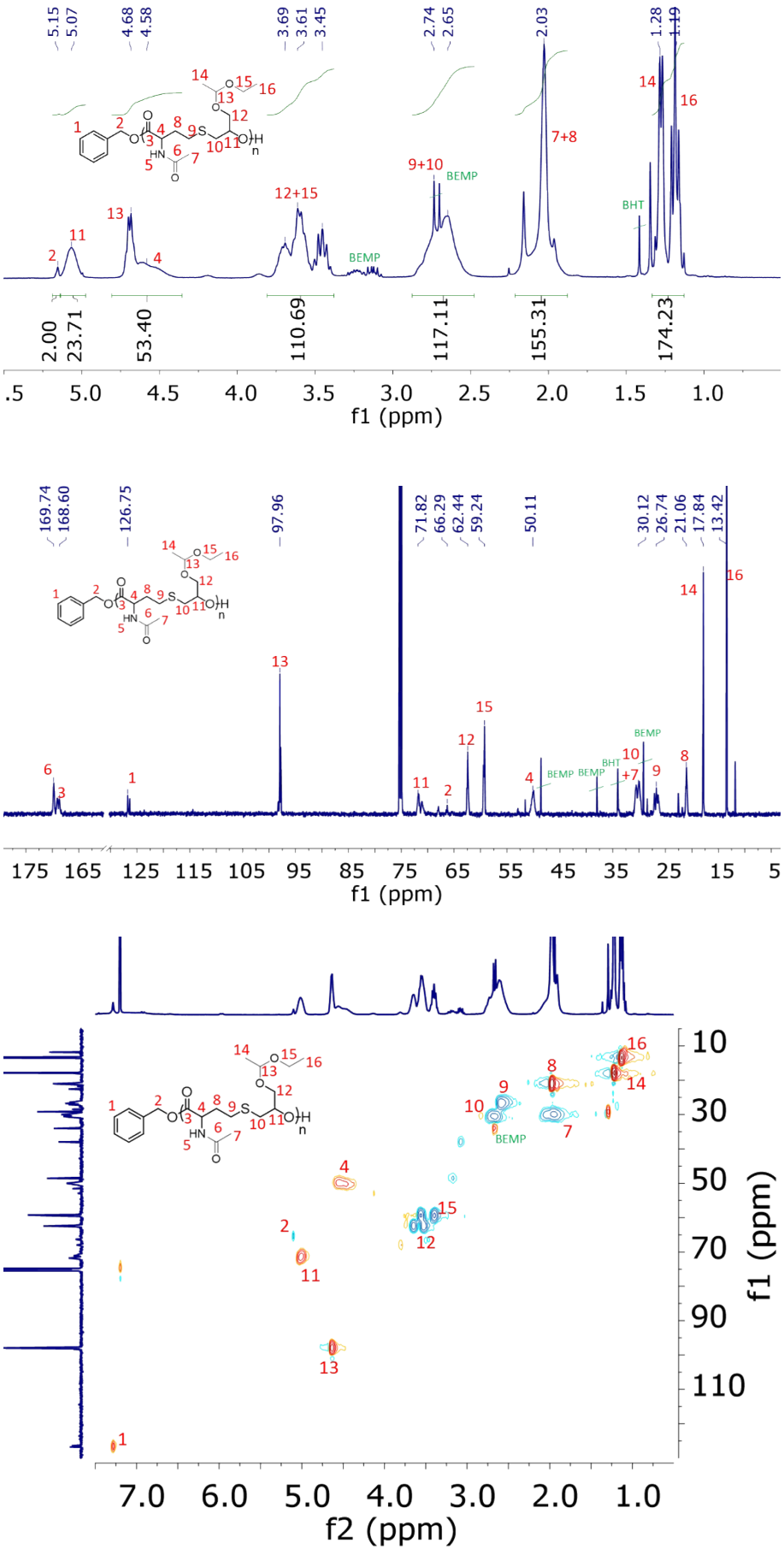
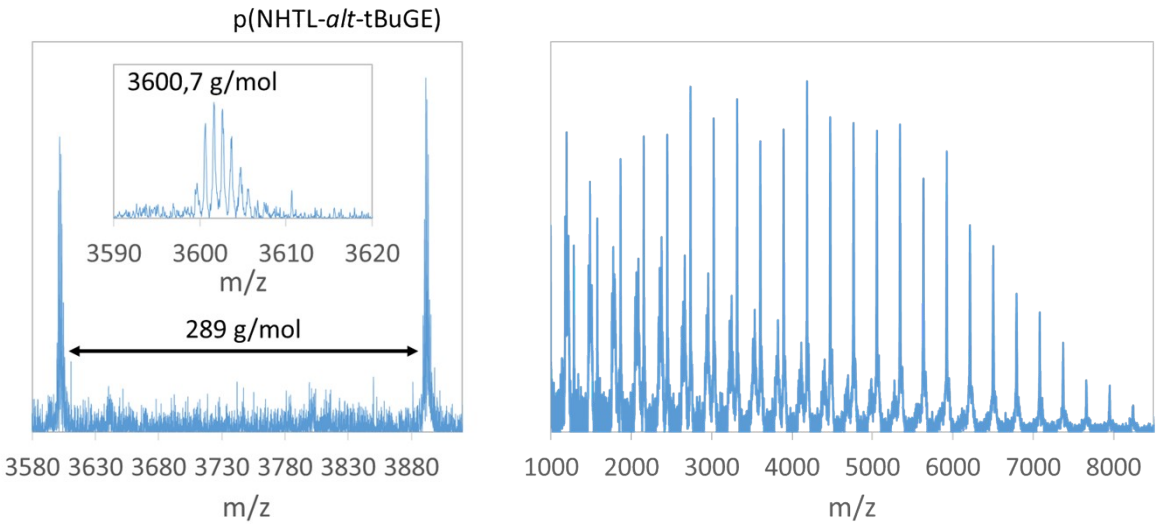


Figure S4: ^{1}H, ^{13}C and HSQC NMR spectrum of p(NHTL-*alt*-*EEGE*) (run 3, table 1) in $CDCl_3$ at 25°C.



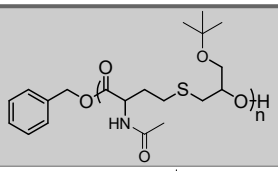
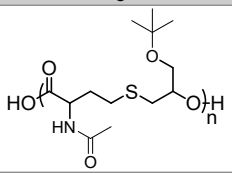
Structure	Cation	Xn	Calculated mass (g/mol)	m/z Maldi-ToF
	Na^+	12	3600,62	3600,7 (R)
	Na^+	13	3799,75	3797,8 (L)

Figure S5: MALDI–ToF analysis of p(NTHL-*alt*-*t*BuGE) (run 2, table 1), reflectron mode on the left and linear mode on the right.

Equation E1: Determination method of the degradation rate.

The degradation rate of a polymer chain is determined by SEC using the following method.

After reaction, the average molar mass in number $M_n(t)$ of the sample is determined by (1) as a function of the molar mass before degradation $M_n(0)$, and the number of macromolecules formed after methanolysis of the esters, i.e. the average number of broken ester function(s) per chain plus 1. This then corresponds to the difference between the average number of ester bonds N_{ester} per macromolecular chain before degradation ($N_{ester,0}$) and after degradation ($N_{ester}(t)$) and this difference can be less than 1 at the beginning of the degradation.

$$M_n(t) = \frac{M_n(0)}{\left(N_{ester,0} - N_{ester}(t)\right) + 1} \quad (1)$$

It is therefore possible to express the number of ester bonds after degradation. (2)

$$N_{ester}(t) = \frac{M_n(t) * \left(1 + N_{ester,0}\right) - M_n(0)}{M_n(t)} \quad (2)$$

The percentage degradation of a poly(ester-alt-thioether) chain is given by formula (3) :

$$\%Deg = 1 - \frac{N_{ester}(t)}{N_{ester,0}} \quad (3)$$

In addition, the number of ester bonds in the polymer chain before degradation is equal to the number of repeating units minus one, i.e. the ratio between the molar mass before degradation $M_n(0)$ and the molar mass of a repeating unit M_0 (determined by SEC after total degradation) minus one (4).

$$N_{ester,0} = \frac{M_n(0)}{M_0} - 1 \quad (4)$$

Expressing the rate of degradation (3) as a function of (2) and (4) gives (5) :

$$\%Deg = 1 - \frac{M_n(t)\left(1 + \frac{M_n(0)}{M_0} - 1\right) - M_n(0)}{M_n(t) * \left(\frac{M_n(0)}{M_0} - 1\right)} \quad (5)$$

This gives the formula for the rate of degradation (6) after calculation and simplification of the expression :

$$\%Deg = 1 - \frac{M_n(0) * (M_n(t) - M_0)}{M_n(t) * (M_n(0) - M_0)} \qquad (6)$$

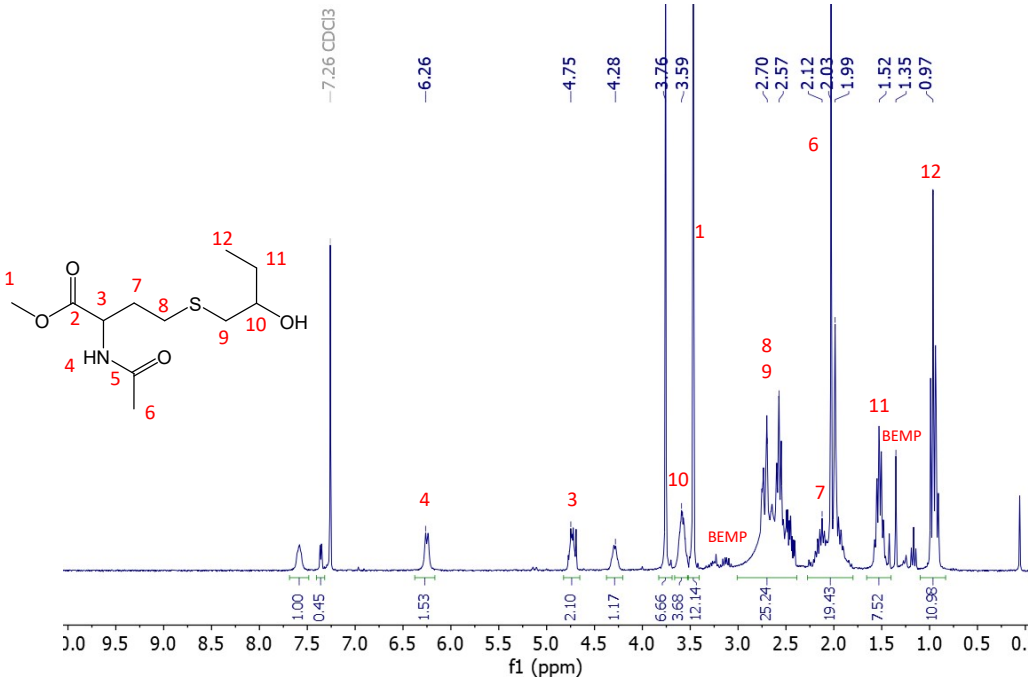


Figure S6. ^{1}H NMR spectrum of degraded p(NHTL-*alt*-BO) (run 1, table 1) before purification by silica column chromatography in $CDCl_3$ at 25°C.

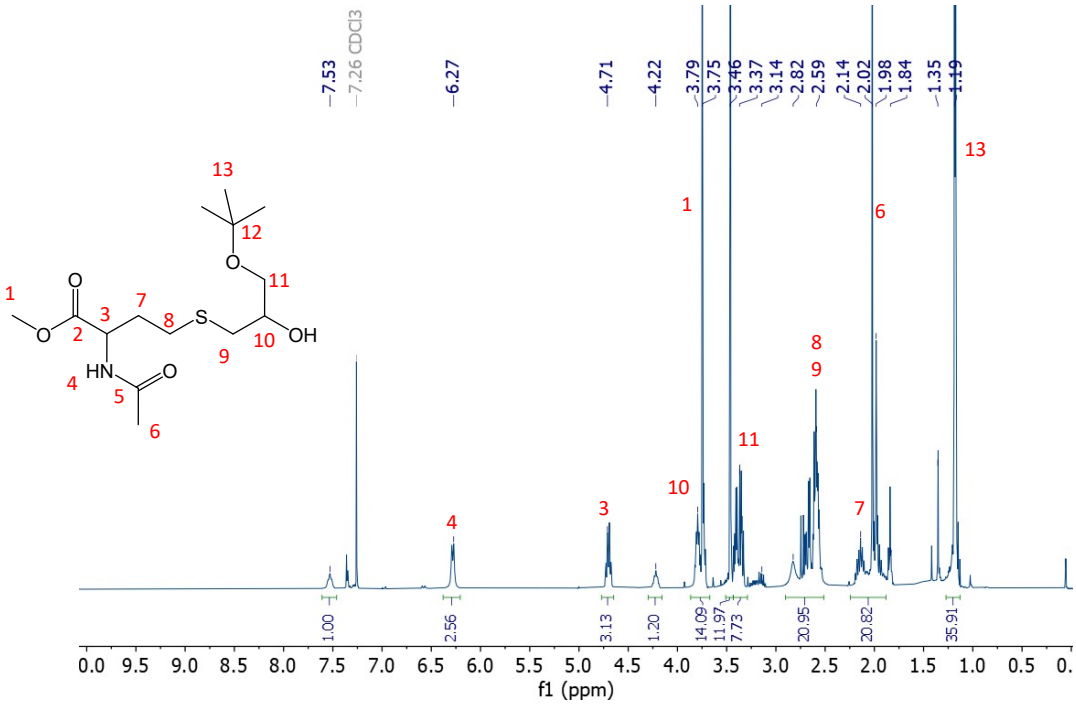


Figure S7. ^{1}H NMR spectrum of degraded p(NHTL-*alt*-*t*BuGE) (run 2, table 1) before purification by silica column chromatography in $CDCl_3$ at 25°C.

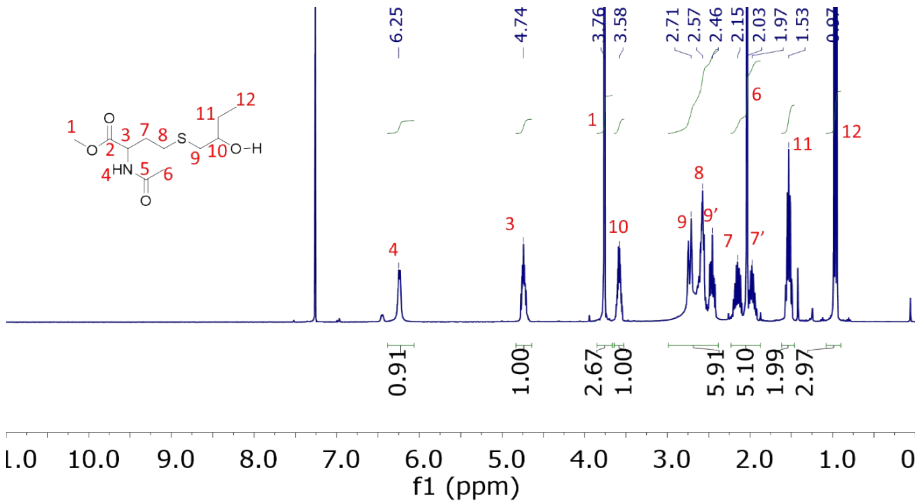


Figure S8: Full ^{1}H NMR spectrum of degraded p(NHTL-alt-BO) (run 1, table 1) in $CDCl_3$ at 25°C.

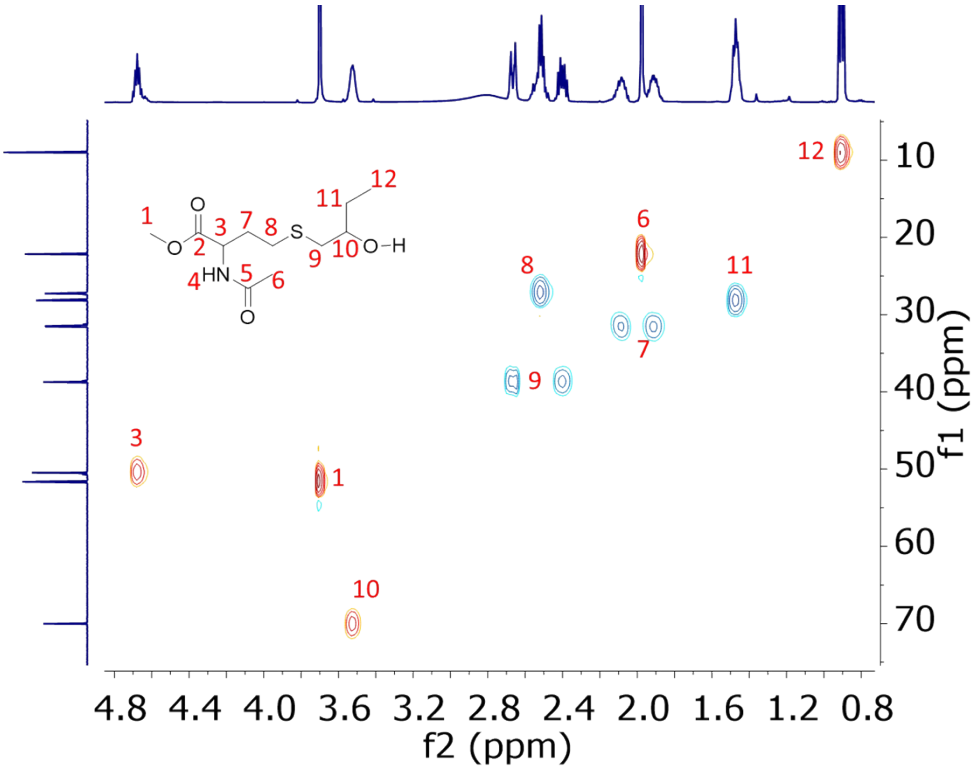


Figure S9: HSQC NMR spectrum of degraded p(NHTL-alt-BO) (run 1, table 1) in $CDCl_3$ at 25°C.

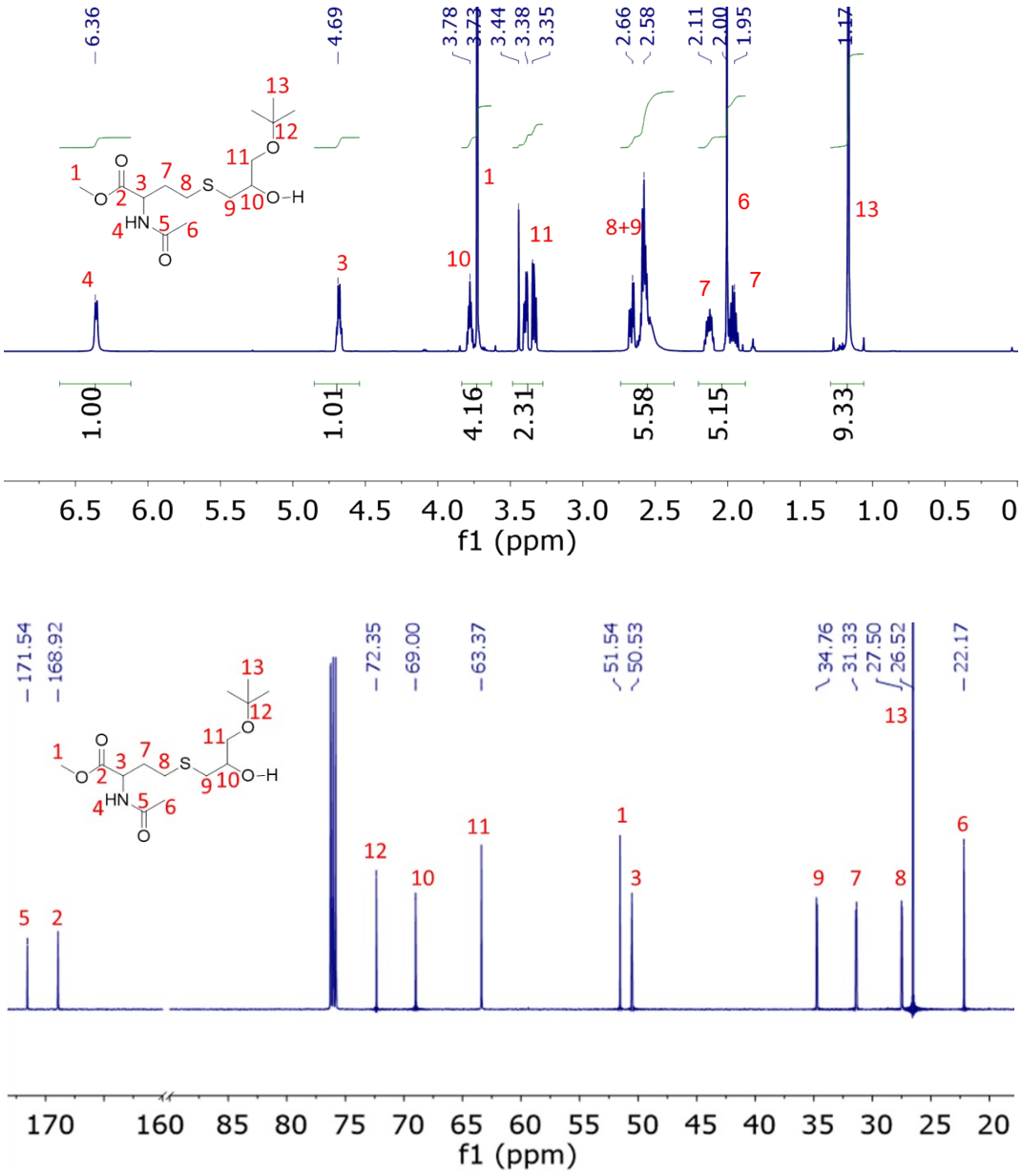


Figure S10: ^{1}H (up) and ^{13}C (bottom) NMR spectrum of degraded p(NHTL-*alt*-*t*BuGE) (run 2, table 1) in $CDCl_3$ at 25°C.

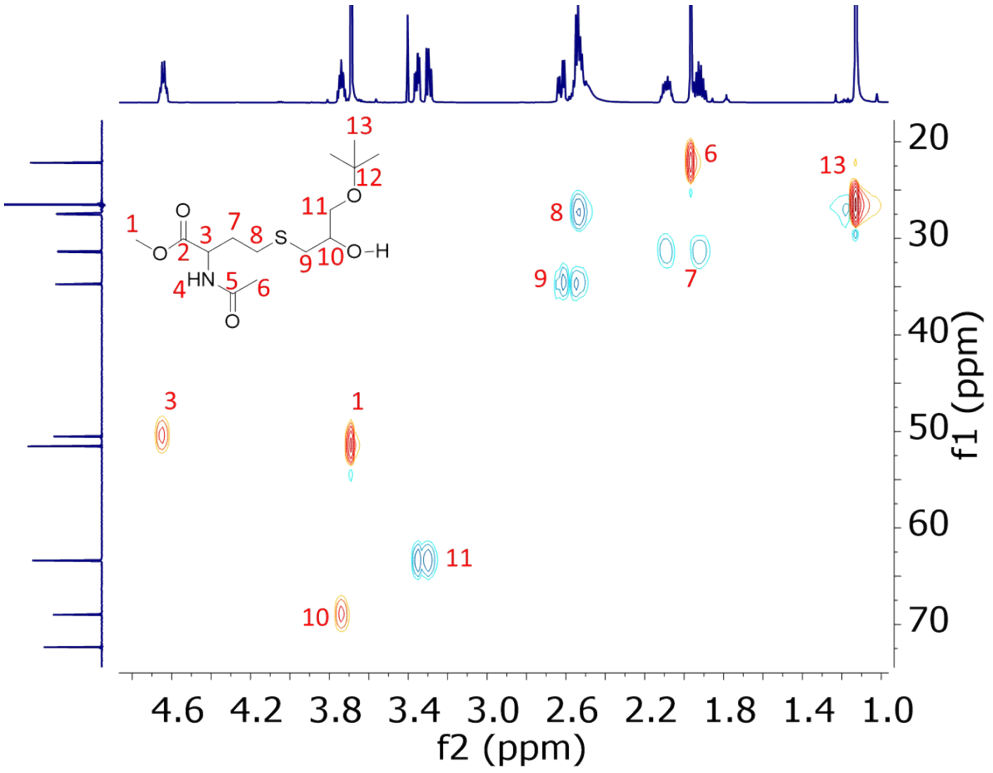


Figure S11: HSQC NMR spectrum of degraded p(NHTL-*alt*-*t*BuGE) (run 2, table 1) in $CDCl_3$ at 25°C.

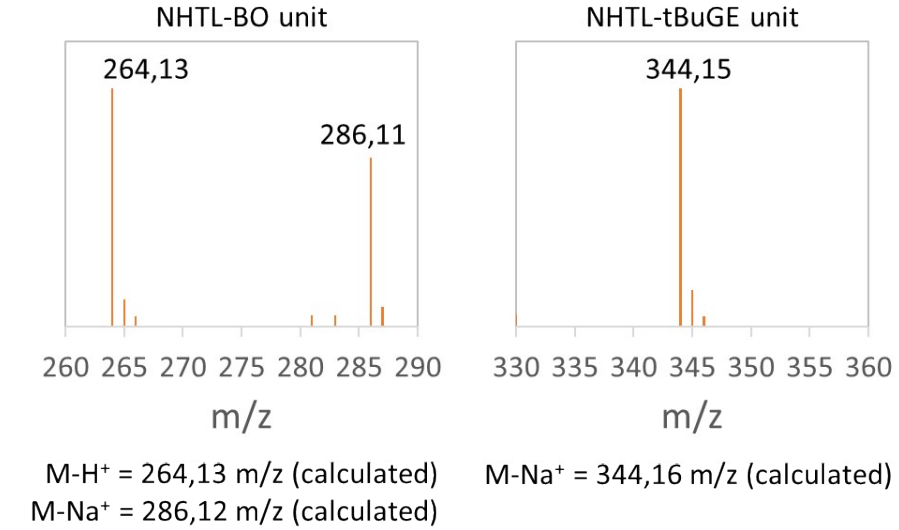


Figure S12: HRMS-ESI analysis of NHTL-BO unit (run 1, table 1 degraded on the left) and NHTL-*t*BuGE unit (run 2, table 1 degraded on the right).

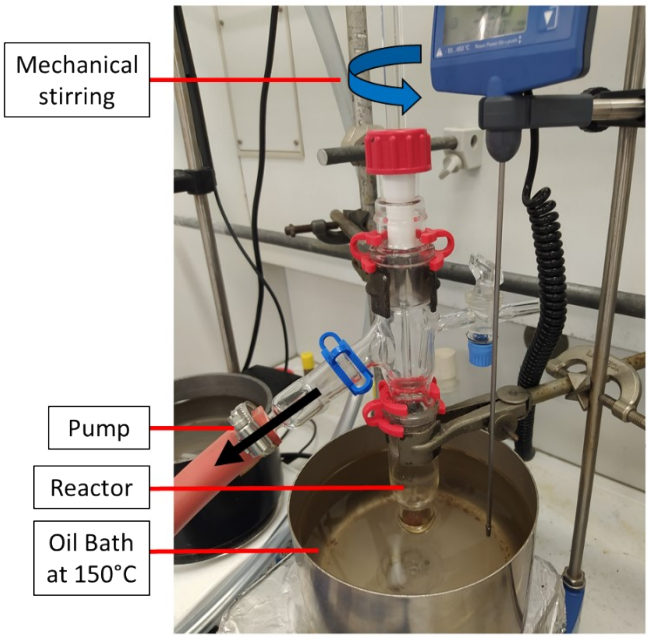


Figure S13: Photo of the polycondensation reactor

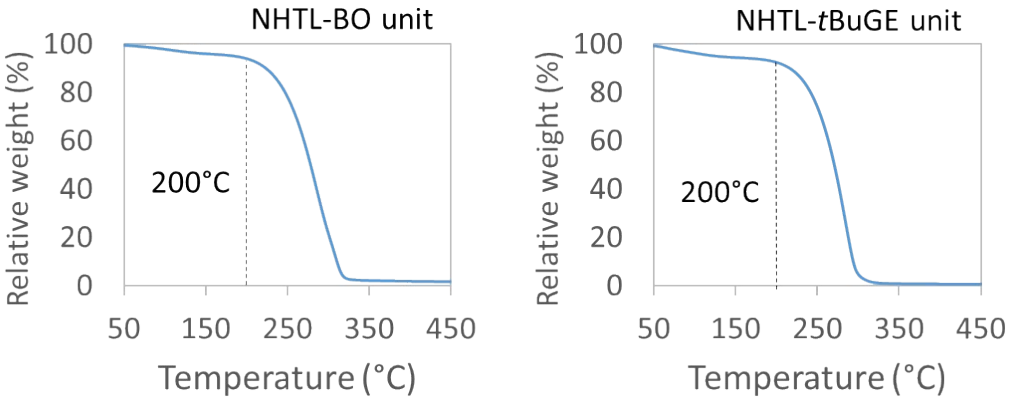


Figure S14: TGA analysis of NHLT-BO unit (on the left) and NHTL-*t*BuGE unit (on the right)

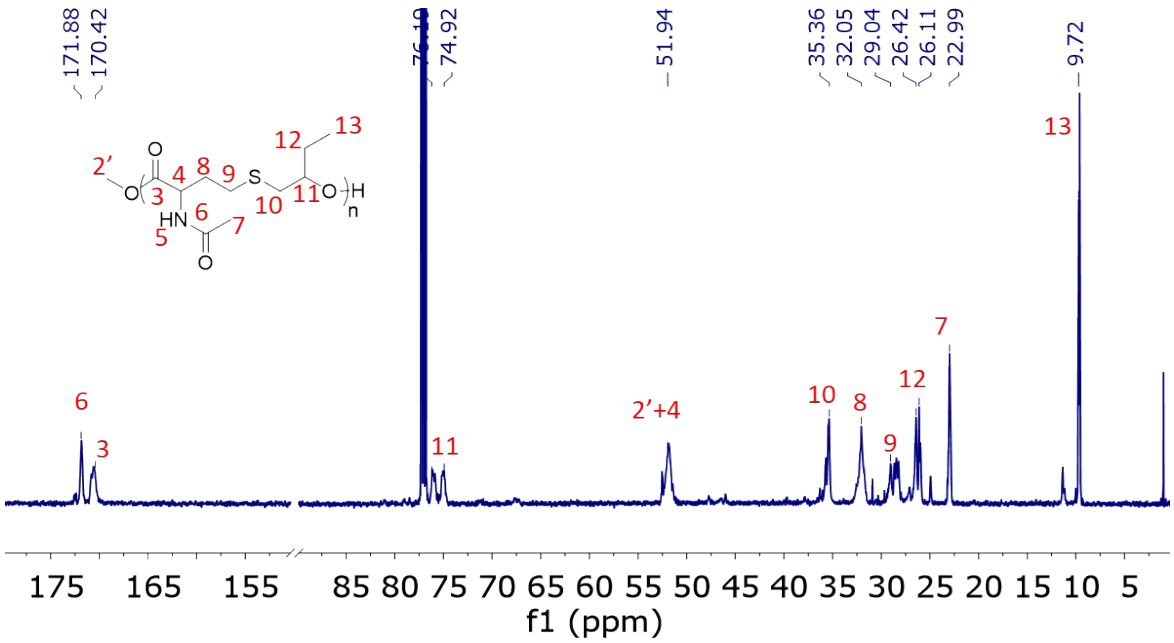


Figure S15: ^{13}C NMR spectrum of p(NHTL-*alt*-BO) synthesized by polycondensation (run 7, table 3) in $CDCl_3$ at 25°C.

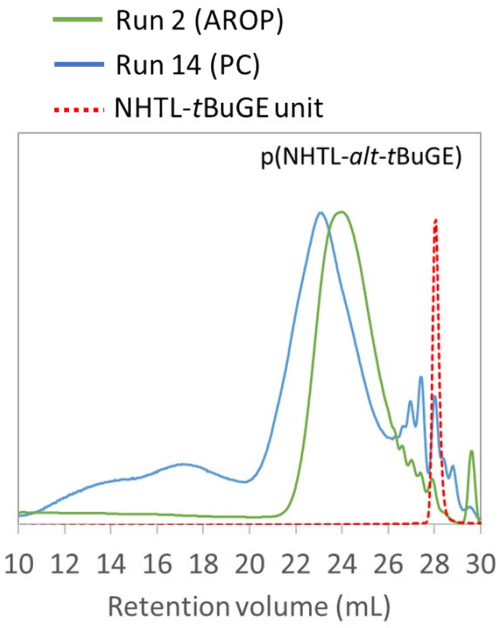


Figure S16: SEC analysis of p(NHTL-*alt*-*t*BuGE) synthesized by AROP (run 2, table 1 in green) and PC (run 14, table 3 in blue) in THF at 40°C.

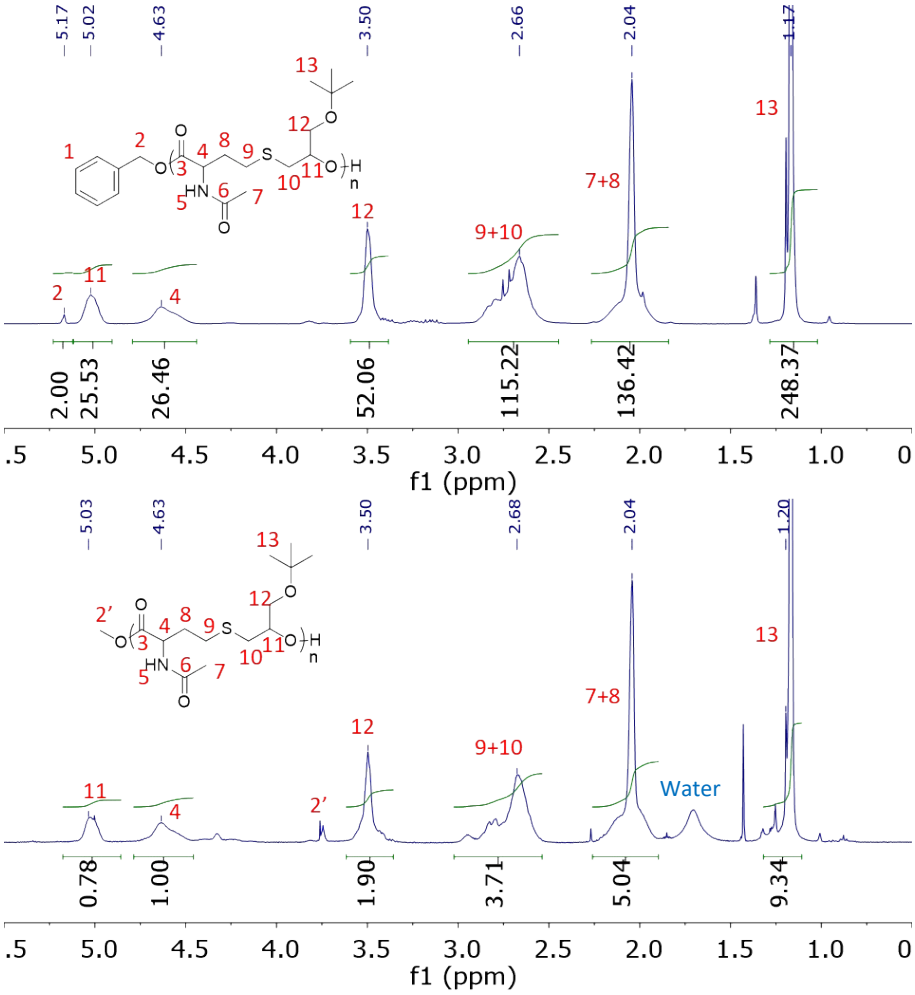
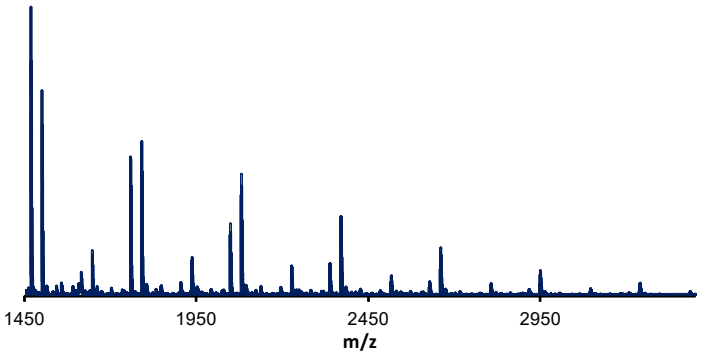
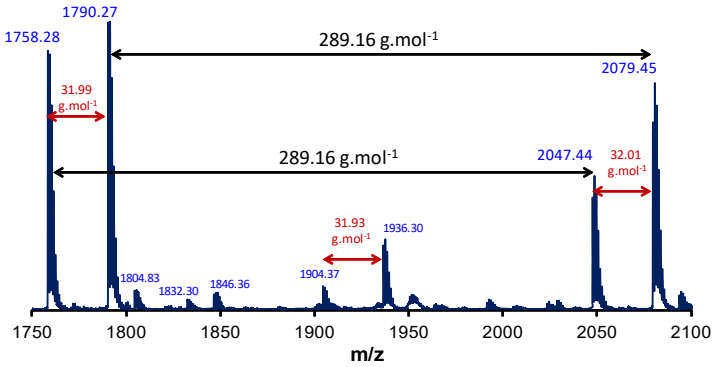
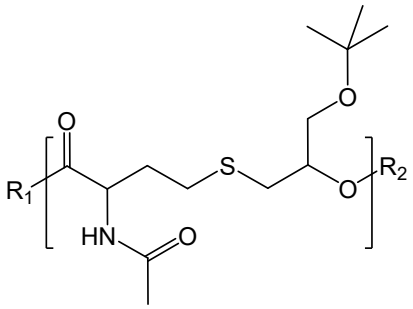


Figure S17: ^{1}H NMR analysis in $CDCl_3$ at 25°C of p(NHTL-*alt*-*t*BuGE) synthesized by AROP (run 2, table 1, top) and polycondensation (run 14, table 3, bottom)







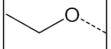
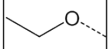
R_1	R_2	Cation	X_n	Calculated mass (g/mol)	Experimental mass (g/mol)
Macrocycle		Na^+	6	1757.83	1758.28
	H	Na^+	6	1789.86	1790.27
	H	Na^+	6	1803.87	1804.83
		Na^+	6	1831.87	1832.3
		Na^+	6	1845.88	1846.36

Figure S18: MALDI–ToF analysis of p(NTHL-*alt*-tBuGE) (run 14, table 3), reflectron mode on the left and linear mode on the right.

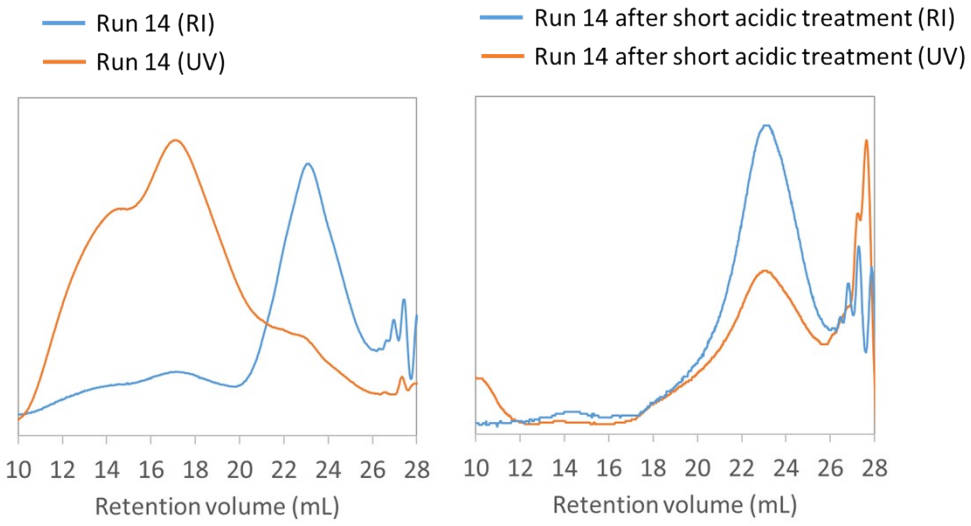


Figure S19: SEC analysis (RI and UV signals) of p(NHTL-*alt*-*t*BuGE) (run 14, table 3) before (on the left) and after (on the right) a 30min HCl treatment at 10^{-1}M in THF at 40°C.

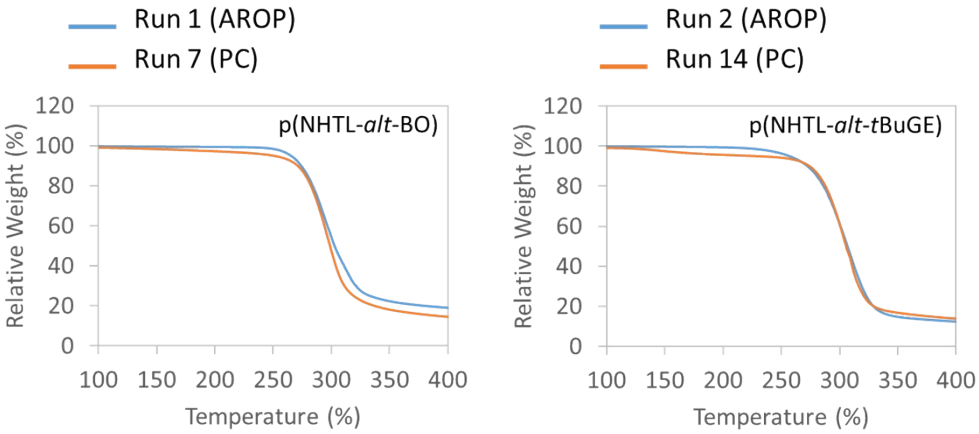


Figure S20: TGA curves of a 10°C/min ramp of poly(ester-*alt*-thioether)s. Superposition of the thermal degradation of p(NHTL-*alt*-BO) on the left and p(NHTL-*alt*-*t*BuGE) on the right with polymers obtained by AROP (run 1 and 2, table 1 in blue) and by PC (run 7 and 14, table 3 in orange).

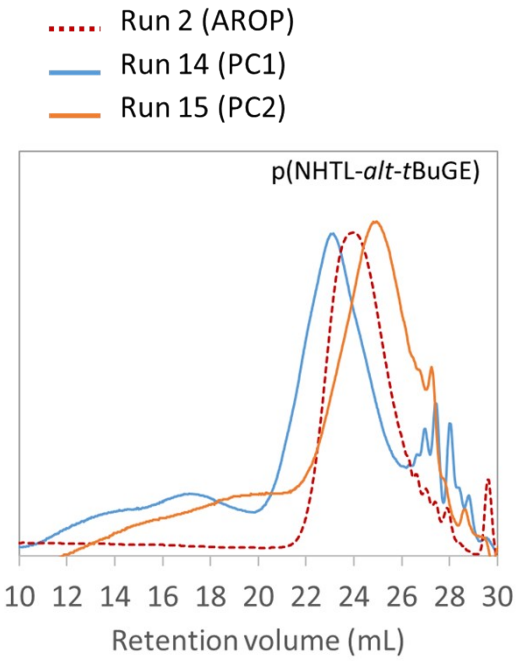


Figure S21: Comparative SEC analysis of p(NHTL-*alt*-*t*BuGE) obtained by AROP (run 2, table 1 in red), first repolymerization (run 14, table 3 in blue) and second repolymerization (run 15, table 3 in orange) in THF at 40°C.

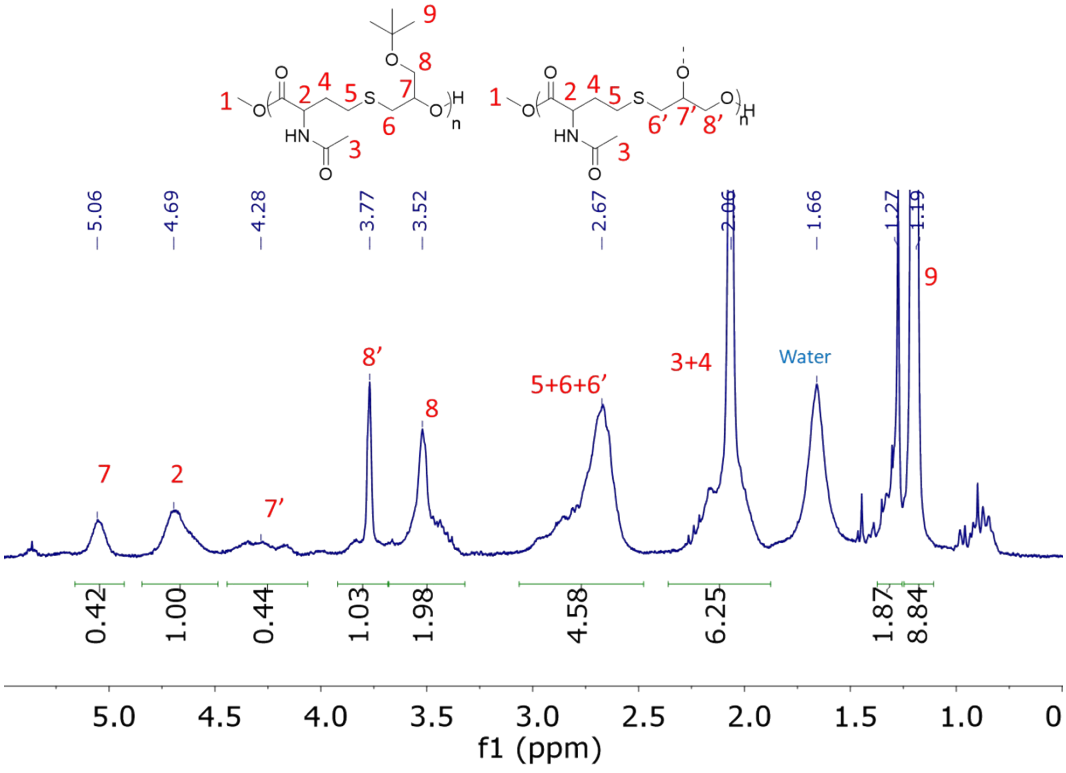


Figure S22: ^{1}H NMR spectrum of p(NHTL-*alt*-*t*BuGE) synthesized by a second polycondensation in presence of $Ti(OBu)_4$ (run 15, table 3) in $CDCl_3$ at 25°C with hypothetical attributions of the branched moiety.