Supporting Information

Bio-based poly(ester-*alt*-thioether)s synthesized by organo-catalyzed ring-opening copolymerizations of eugenol-based epoxides and *N*-acetyl homocysteine thiolactone

Simon Le Luyer,[a] Baptiste Quienne,[b] Matthieu Bouzaid,[a] Philippe Guégan,[a] Sylvain Caillol[b] and Nicolas Illy[a,*]

[a] Sorbonne Université, CNRS, Institut Parisien de Chimie Moléculaire, Equipe Chimie des Polymères, 4 place Jussieu, F-75005 Paris, France.

[b] ICGM, Univ Montpellier, CNRS, ENSCM, Montpellier, France.

Experimental Part

Materials.

Phosphazene base 2-*tert*-butylimino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diazaphosphorine (BEMP) solution (1.0 mol.L^{-1} in hexane, Sigma-Aldrich), 1-tert-Butyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)-phosphoranylidenamino]-2λ5,4λ5-catenadi(phosphazene) (*t*BuP$_4$) solution (0.8 mol.L^{-1} in hexane, Sigma-Aldrich), 4-(dimethylamino)pyridine ($\geq$ 99%, Sigma-Aldrich), benzyl alcohol (99.8 % anhydrous, Sigma-Aldrich), DL-*N*-Acetylhomocysteine thiolactone (98%, Sigma-Aldrich), eugenol (99 %, Sigma-Aldrich), dihydroeugenol (99 %, Sigma-Aldrich), epichlorohydrin (99 %, Sigma-Aldrich), benzyltriethylammonium bromide (99 %, Sigma-Aldrich), 2,2-dimethoxy-2-phenylacetophenone (99 %, Sigma-Aldrich), 2-mercaptoethanol ($\geq$ 99%, Sigma-Aldrich) and vanillin glycidyl ether (Specific Polymers) were used as received. Vanillin monoglycidyl ether. THF was dried with an MBRAUN MB SPS-800 solvent purification system under nitrogen.

Instruments.

^{1}H, ^{13}C NMR and ^{1}H-^{15}N HSQC spectra were recorded in $CDCl_3$ or CD_3COCD_3 using a Bruker 400 MHz NMR spectrometer. *IR spectra* were collected using a Perkin-Elmer Spectrum1000 FTIR infrared spectrometer with a diamond ATR probe. Size Exclusion Chromatography Experiment (SEC) were carried out on three PL gel Mixed-C 5µm columns (7,5 × 300 mm; separation limits: 0,2 to 2000 kg.mol^{-1}) maintained at 40°C and sample Viscotek GPCmax delivery module and 2 modular detectors: a Viscoteck 3580 differential

refractive index (RI) detector and a Shimadzu SPD20-AV diode array UV detector. THF was used as the mobile phase at a flow rate of 1 mL.min^{-1}, toluene was used as a flow rate marker. All polymers were injected (50 µL) at a concentration of 5 mg.mL^{-1} after filtration through a 0.45 µm pore-size membrane. The OmniSEC 4.6.2 software was used for data acquisition and analysis. Number-average molar masses (M_n), weight-average molar masses (M_w) and dispersities were determined by SEC with a calibration curve based on poly(methyl methacrylate) standard, using the RI detector. The *thermal decomposition* was evaluated by thermogravimetric analysis (TGA) using a TA Q50 apparatus. Data were collected using a 20 °C/min ramp to 600 °C. The experiment was run under a stream of nitrogen. *DSC* measurements were carried out using a TA DSC Q2000 calibrated with indium standard. Sample (ca 15 mg) was placed in an aluminum cell and initially cooled at -70°C. Two heating (10 K min^{-1}) - cooling (10 K min^{-1}) cycles were then applied in the −70 to 200 °C temperature range.

Synthesis of dihydroeugenol glycidyl ethe((DEGE):

10 g (60 mmol, 1 eq.) of dihydroeugenol, 1.37 g (6 mmol, 0.1 eq.) of benzyltriethylammonium bromide and 55,66 g (600 mmol, 10 eq.) of epichlorohydrine were added to a 250 mL round-bottom flask. The mixture was heated at 80 °C for 5 h under stirring. Then, 21 g of 40 wt% NaOH solution (210 mmol, 3.5 eq.) were added and the reaction was left for 1 h at 80 °C. Once the solution was back to room temperature, the solution was filtered to remove the salt formed after the NaOH addition. 200 mL of $CHCl_3$ were then added to the solution and liquid extraction were performed with H_2O and then with brine. After the addition of $MgSO_4$ and filtration, the product was dried under vacuum. To remove the few impurities, the dried product was solubilized in 95:5 cyclohexane/ethyl acetate and purified by flash chromatography starting from 95:5 to 90:10 cyclohexane/ethyl acetate. The pure product was then dried under vacuum and a white powder was obtained (yield = 77 %).

^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 0.93 (t, CH_3), 1.62 (m, CH_2), 2.53 (t, CH_2), 2.72-2.89 (m, CH_2), 3.38 (m, CH), 3.86 (s, CH_3), 4.00-4.22 (m, CH_2), 6.68-6.86 (m, CH_{ar}).

^{13}C NMR (101 MHz, $CDCl_3$): δ/ppm = 13.87 (CH_2-$\underline{C}H_3$), 24.75 (CH_2-$\underline{C}H_2$-CH_3), 37.73 (C-$\underline{C}H_2$-CH_2), 45.05 (O-$\underline{C}H_2$-CH), 50.28 (CH_2-$\underline{C}$H-CH_2), 55.92 ($\underline{C}$H3–O), 70.50 (O-$\underline{C}H_2$-CH), 112.41 (C-$\underline{C}H_{ar}$-C), 114.41 (C-$\underline{C}H_{ar}$-CH_{ar}), 120.70 (C-$\underline{C}H_{ar}$-CH_{ar}), 136.81 (CH_{ar}-$\underline{C}$-CH_{ar}), 146.04 (CH_{ar}-$\underline{C}$-O), 149.44 (CH_{ar}-$\underline{C}$-O).

Synthesis of eugenol glycidyl ether (EGE):

10 g (61 mmol, 1 eq.) of eugenol, 1.38 g (6 mmol, 0.1 eq.) of benzyltriethylammonium bromide and 58,17 g (609 mmol, 10 eq.) of epichlorohydrine were added to a round-bottom flask. The mixture was heated at 80 °C for 5 h under stirring. Then, 21.3 g of 40 wt% NaOH solution (213 mmol, 3.5 eq.) were added and the reaction was left for 1 h at 80 °C. Once the solution was back to room temperature, the solution was filtered to remove the salt formed after the NaOH addition. 200 mL of $CHCl_3$ were then added to the solution and liquid extraction were performed with H_2O and then with brine. After the addition of $MgSO_4$ and filtration, the product was dried under vacuum. To remove the few impurities, the dried product was solubilized in 95:5 cyclohexane/ethyl acetate and purified by flash chromatography starting from 95:5 to 90:10 cyclohexane/ethyl acetate. The pure product was then dried under vacuum and a white powder was obtained (yield = 64 %).

^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 2.72-2.89 (m, CH_2), 3.33 (d, CH_2), 3.37 (m, CH), 3.85 (s, CH_3), 4.00-4.22 (m, CH_2), 5.04-5.10 (m, CH_2), 5.89-6.00 (m, CH), 6.69-6.87 (m, CH_{ar}).

^{13}C NMR (101 MHz, $CDCl_3$): δ/ppm = 39.82 ($C\text{-}\underline{C}H_2\text{-}CH$), 45.05 ($O\text{-}\underline{C}H_2\text{-}CH$), 50.28 ($CH_2\text{-}\underline{C}H\text{-}CH_2$), 55.92 ($\underline{C}$H3–O), 70.50($O\text{-}\underline{C}H_2\text{-}CH$), 112.5 ($C\text{-}\underline{C}H_{ar}\text{-}CH_{ar}$), 114.51 ($C\text{-}\underline{C}H_{ar}\text{-}C$), 115.75 ($\underline{C}H_2\text{-}CH$), 120.70 ($C\text{-}CH_{ar}\text{-}CH_{ar}$), 133.98 ($CH_{ar}\text{-}\underline{C}\text{-}CH_{ar}$), 137.55 ($CH_2\text{-}\underline{C}H\text{-}CH_2$), 146.36 ($CH_{ar}\text{-}\underline{C}\text{-}O$), 149.66 ($CH_{ar}\text{-}\underline{C}\text{-}O$).

General copolymerization procedure.

The copolymerization was carried out according to the following typical procedure. 0.3435 g of NHTL (2.157 mmol, 22 eq.), 0.5023 g of DEGE (2.260 mmol, 23 eq.) and 1.0 mL of dried THF were introduced into a polymerization tube (10 mL Pyrex pressure rated vessel, CEM) fitted with a natural rubber folding skirt stoppers (Saint-Gobain Performance Plastics™). Then, 10 µL of benzyl alcohol (0.097 mmol, 1 eq.) and 100 µL of BEMP solution (0.100 mmol, 1 eq.) were added through the septum using a 10 µL and a 100 µL Hamilton™ Gastight™ 1700 Series microsyringes. Then, the reaction mixture was stirred (300 rpm) at 55 °C in an oil bath. and left to react for the required period of time. The progress of the reaction was monitored by removing samples from the polymerization reactor through a septum using fine dosage syringes (Injekt®-F Solo) equipped with Sterican® single-use needles (B-Braun) at various reaction times for 1H NMR analyses. The polymerization was quenched by adding 100 µL of ethanol in the reaction mixture. After removing residual monomers and solvent by rotary evaporation, the polymer was dissolved in 60 mL of methanol and dialyzed in cellulose ester membrane (Repligen Spectra/Por 6 dialysis tubing, flat width = 45 mm, molecular cutoff = 1 kDa) against 600 mL of methanol for 24 hours (the methanol dialysate was changed 3 times). After removing the solvent under vacuum at 50 °C a white solid was obtained and dried overnight under vacuum in an oven at 60°C. Yield: 85 %. Deviations from this general procedure are summarized in Table 1.

Thiol-ene photoinitiated reaction

In a glovebox, 0.5 g of poly(NHTL-*alt*-EGE) (Table 1, run 15; 1.32 mmol of allyl groups, 1 eq.), 0.515 g of 2-mercaptoethanol (6.6 mmol, 5 equivalents per allyl) and 0.068 g of 2,2-dimethoxy-2-phenylacetophenone (0.264 mmol, 0.2 equivalents per allyl) were dissolved in 7.0 mL of dry THF in a glovebox. The stirred mixture was irradiated by UV light at 365 nm for 20 min. The polymer was recovered by dialysis against chloroform. Yield: 90 %.

Table S1. Water content in the monomers determined by Karl Fischer titration method.

	Water content (ppm)
THF	17
NHTL	598
DEGE	363
EGE	796

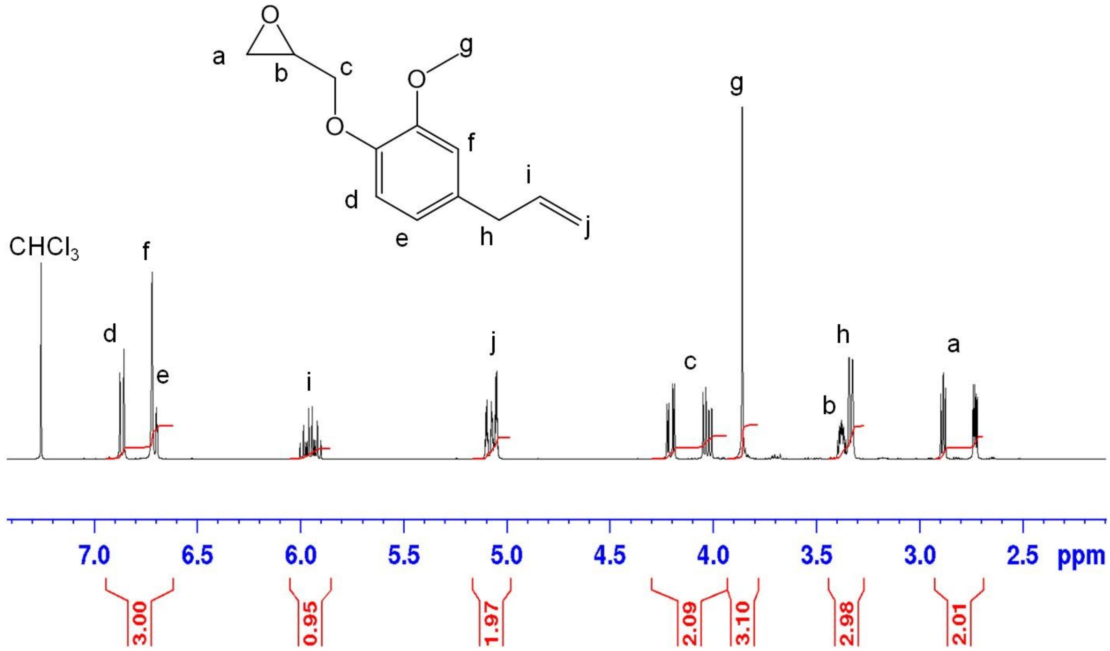


Figure S1. ^{1}H NMR spectrum of EGE in CDCl$_3$ at room temperature.

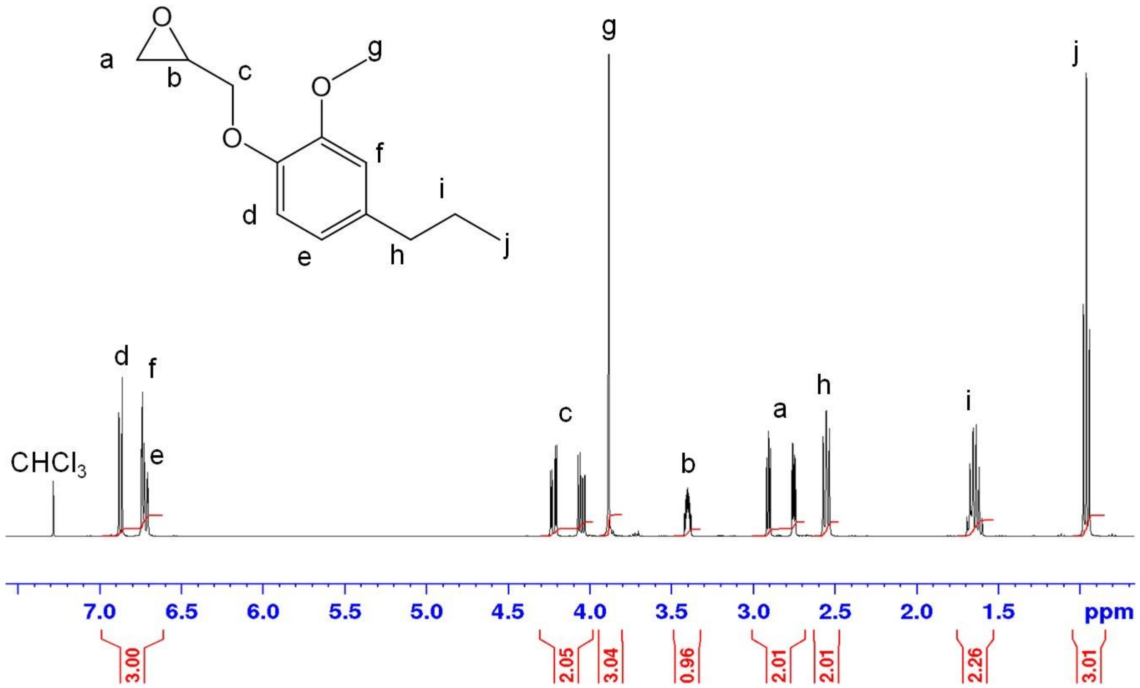


Figure S2. ^{1}H NMR spectrum of DEGE in CDCl$_3$ at room temperature.

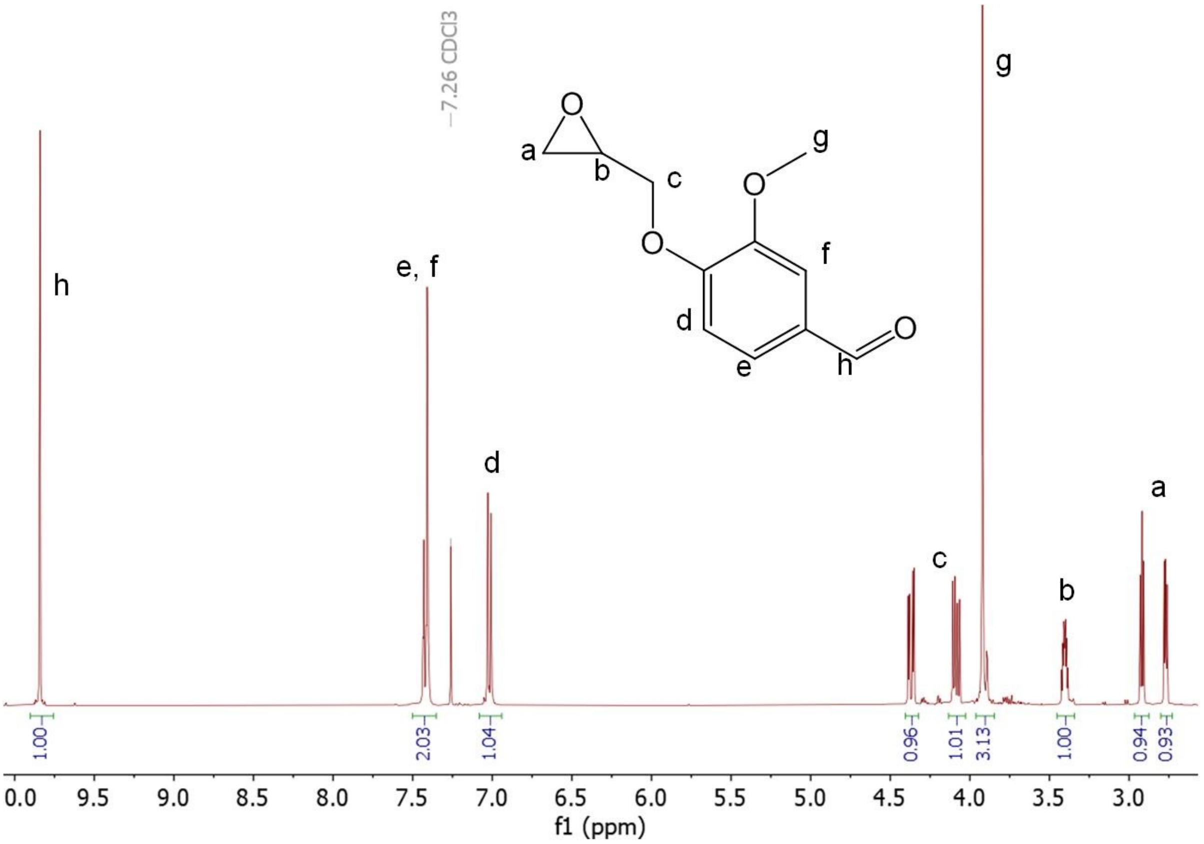
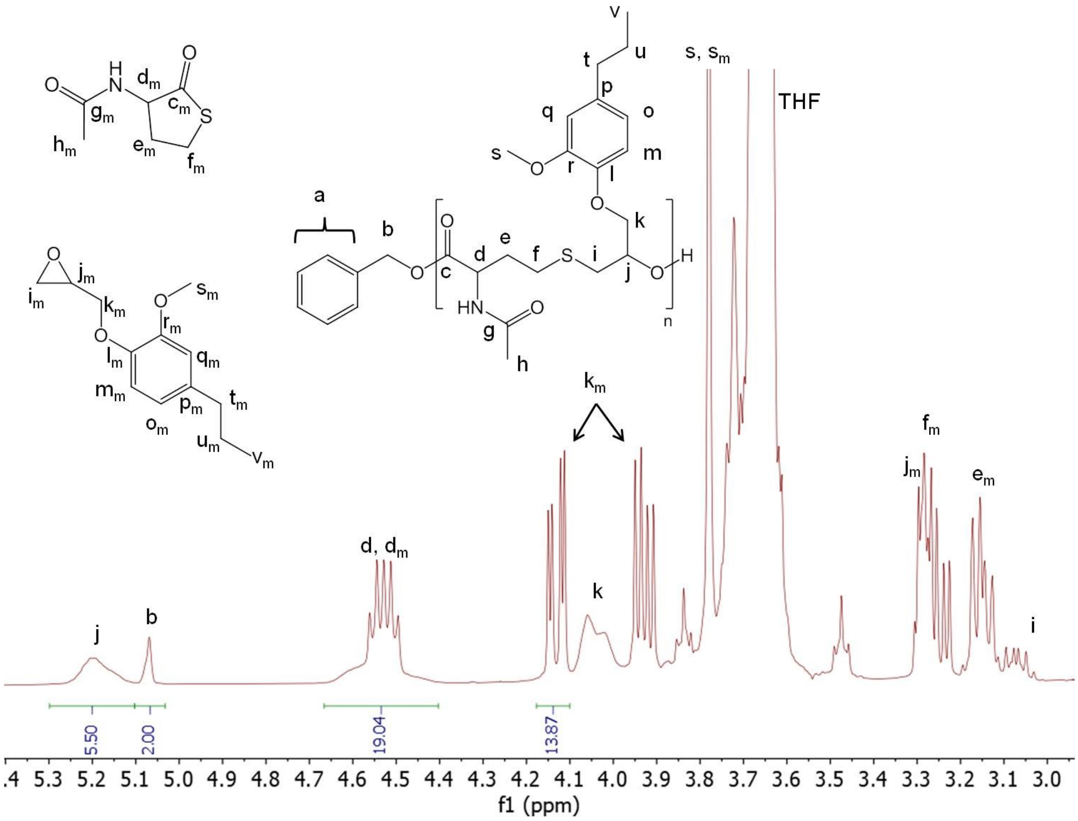


Figure S3. ^{1}H NMR spectrum of VGE in CDCl$_3$ at room temperature.



$$Cv_{NTBL} = \frac{I_j + {}^{I_B}/_{2}}{I_d + I_{d_m}} \times 100$$

$$Cv_{epo} = \frac{I_j + {}^{I_B}/_{2}}{I_j + {}^{I_B}/_{2} + {}^{I_{k_m}}/_{2}} \times 100$$

Figure S4. 1H NMR spectrum of the reaction mixture of a copolymerization between DEGE and NHTL initiated by benzyl alcohol-BEMP in THF at 55°C after 6 h (Table 1, run 9).

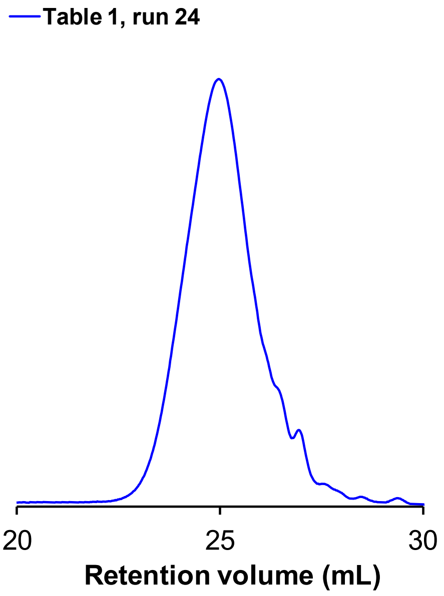


Figure S5. SEC profile in THF of poly(NHTL-*alt*-VGE) initiated by benzyl alcohol-BEMP synthesized in THF at 55 °C (Table 1, run 24).

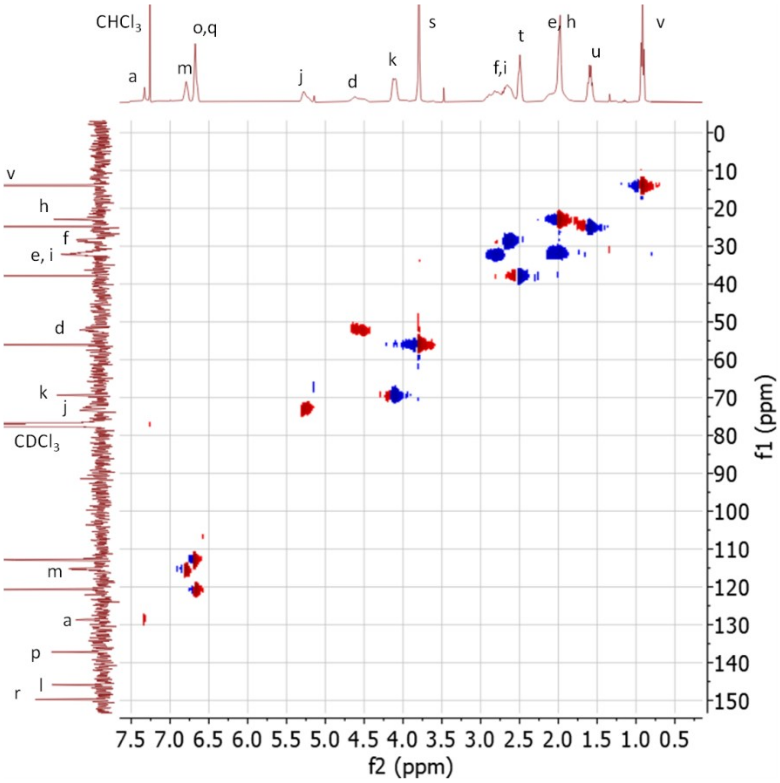


Figure S6 2D HSQC-NMR spectrum in CDCl3 at room temperature of a poly(NHTL-*alt*-DEGE) (Table 1, run 5).

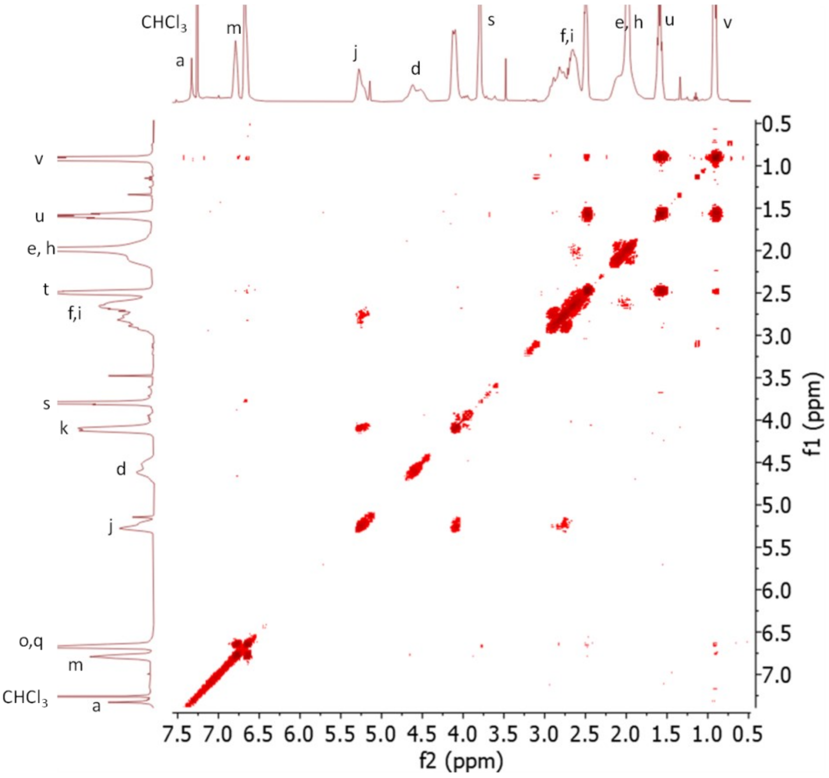


Figure S7. 2D COSY-NMR spectrum in CDCl3 at room temperature of a poly(NHTL-*alt*-DEGE) (Table 1, run 5).

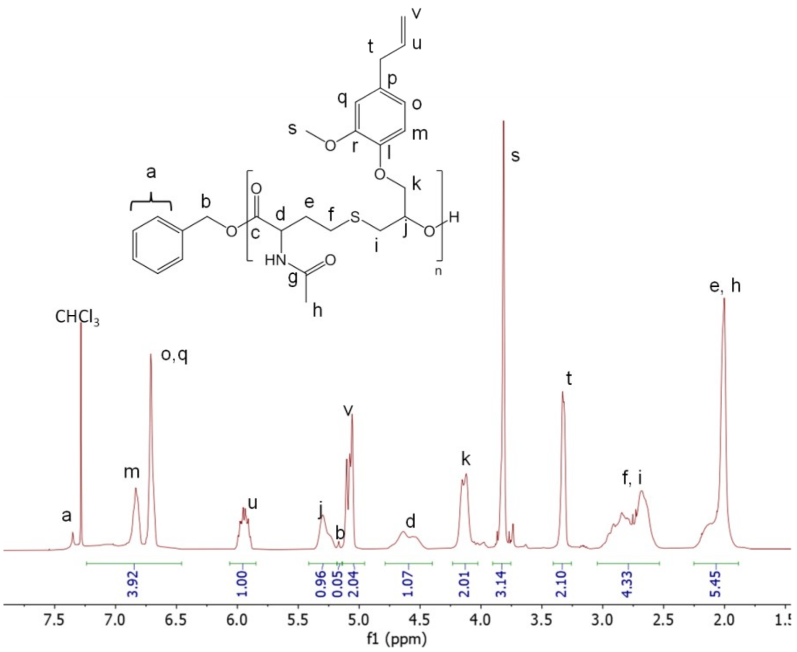


Figure S8. ^{1}H NMR spectrum of poly(NHTL-*alt*-EGE) in $CDCl_3$ at 25°C (Table 1, run 10).

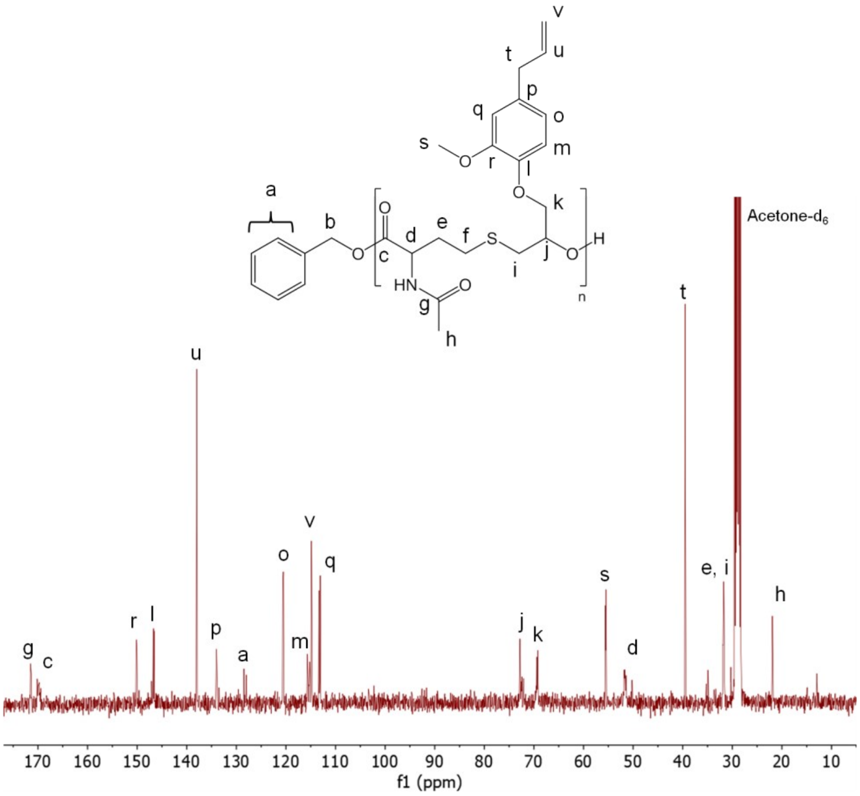


Figure S9. ^{13}C NMR spectrum of poly(NHTL-*alt*-EGE) in acetone-d_6 at 25°C (Table 1, run 10).

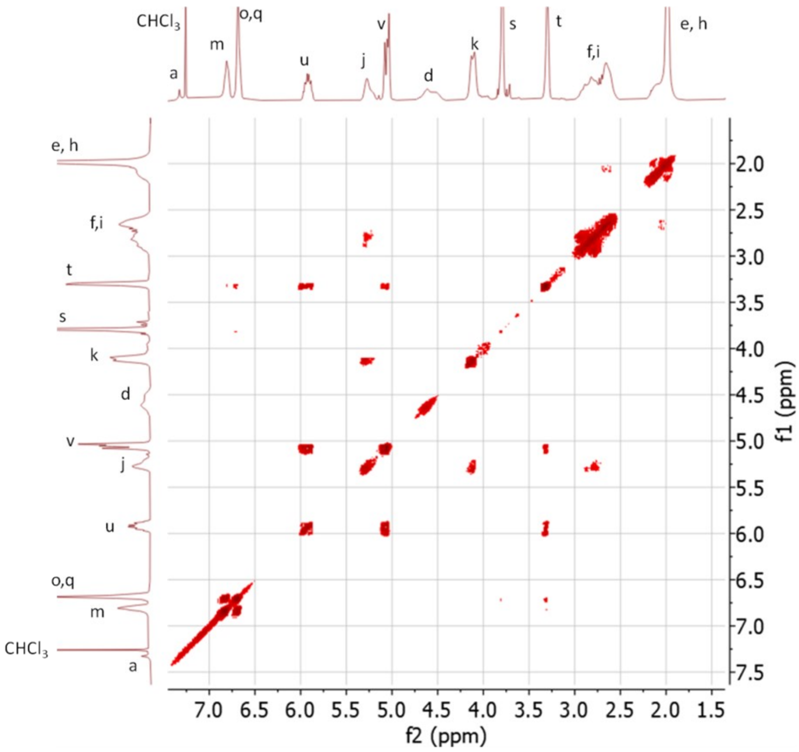


Figure S10. 2D COSY-NMR spectrum in $CDCl_3$ at room temperature of a poly(NHTL-*alt*-EGE) (Table 1, run 10).

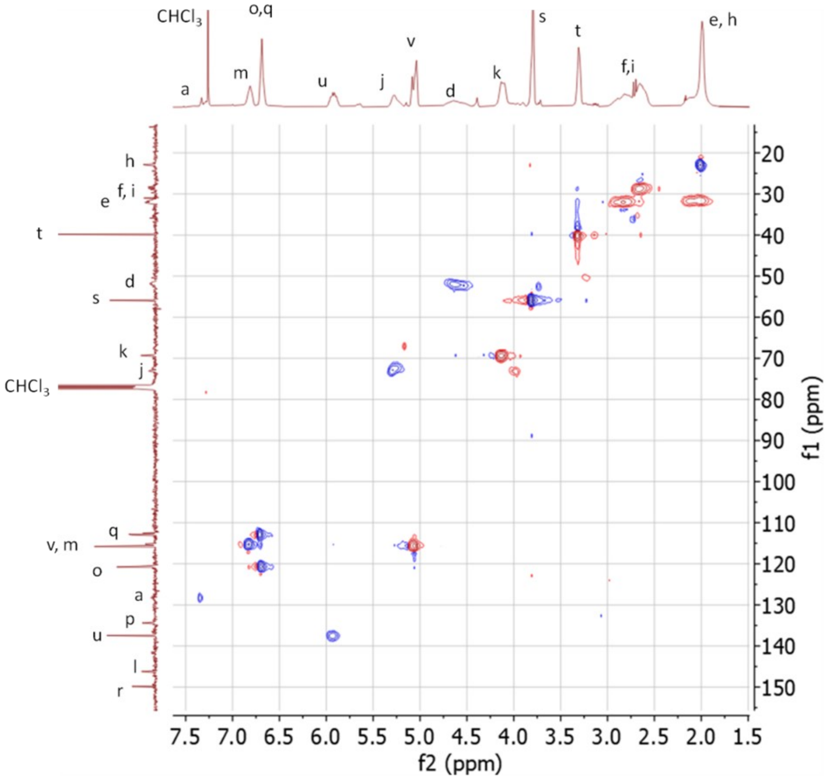


Figure S11. 2D HSQC-NMR spectrum in $CDCl_3$ at room temperature of a poly(NHTL-*alt*-EGE) (Table 1, run 10).

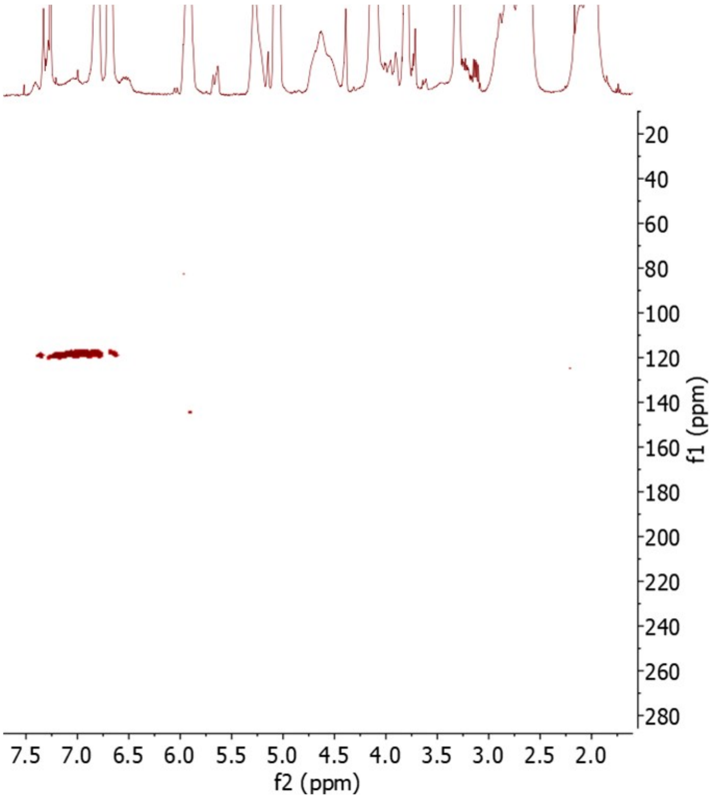


Figure S12. 2D ^{1}H-^{15}N HSQC NMR spectrum in acetone-d_6 at 25 °C of poly(NHTL-*alt*-EGE) (Table 1, run 10).

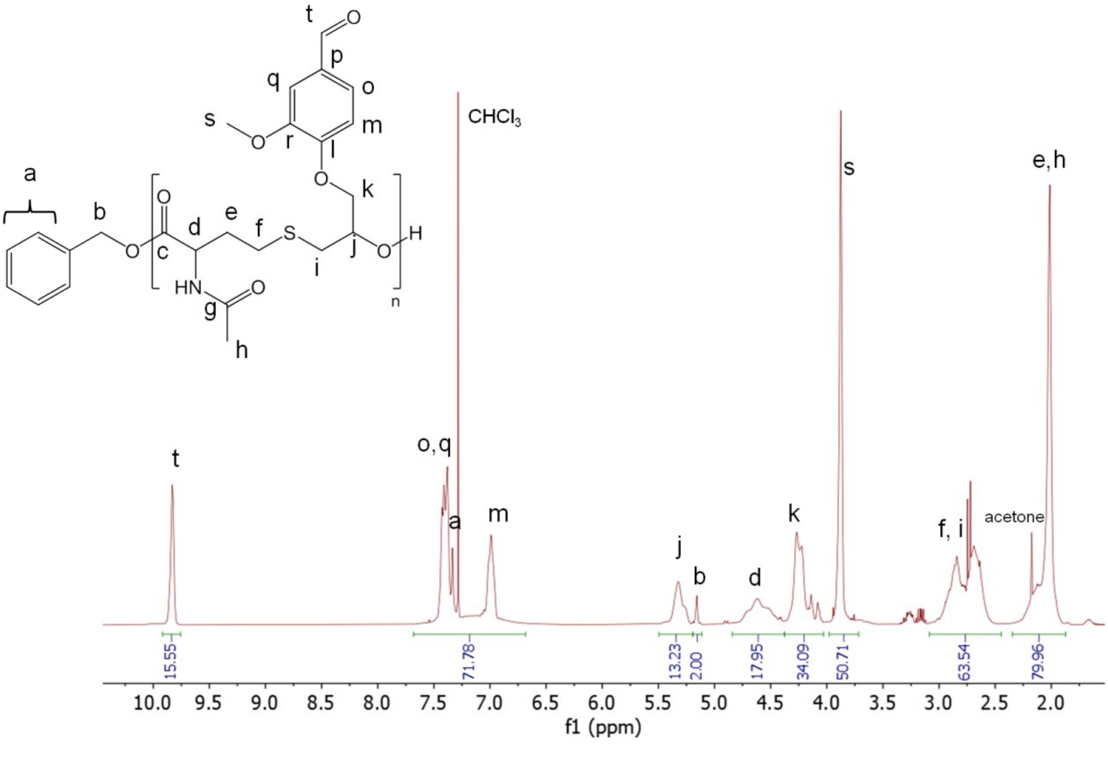


Figure S13. ^{1}H NMR spectrum of poly(NHTL-*alt*-VGE) in $CDCl_3$ at 25°C (Table 1, run 24).

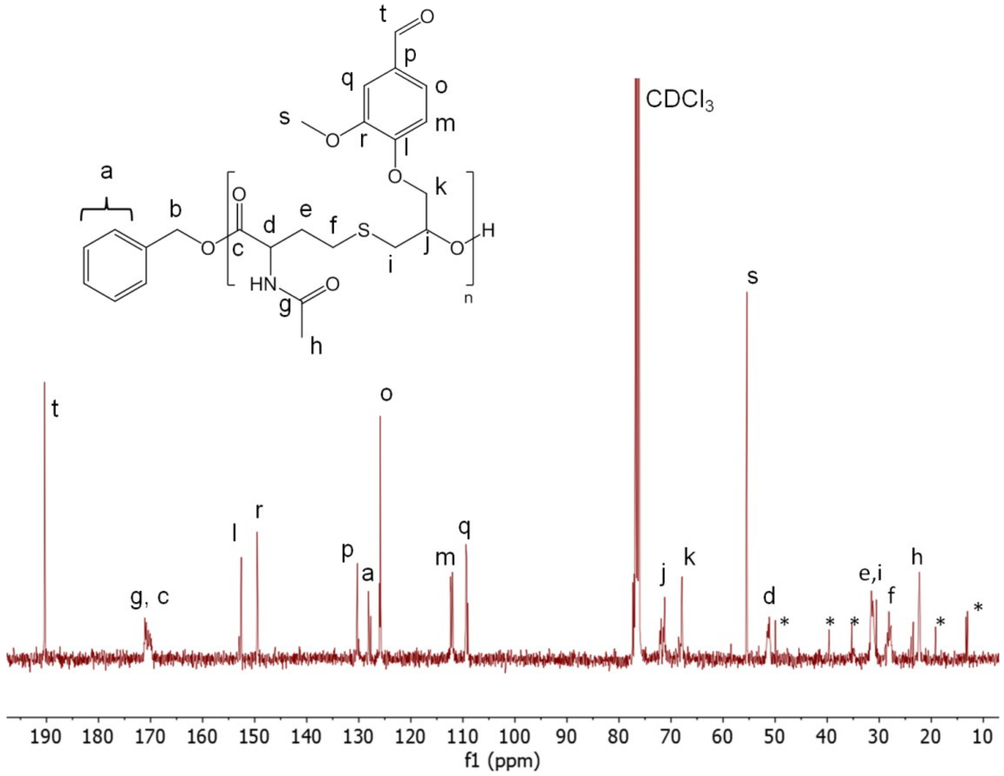


Figure S14. ^{13}C NMR spectrum of poly(NHTL-*alt*-VGE) in acetone-d$_6$ at 25°C (Table 1, run 24).

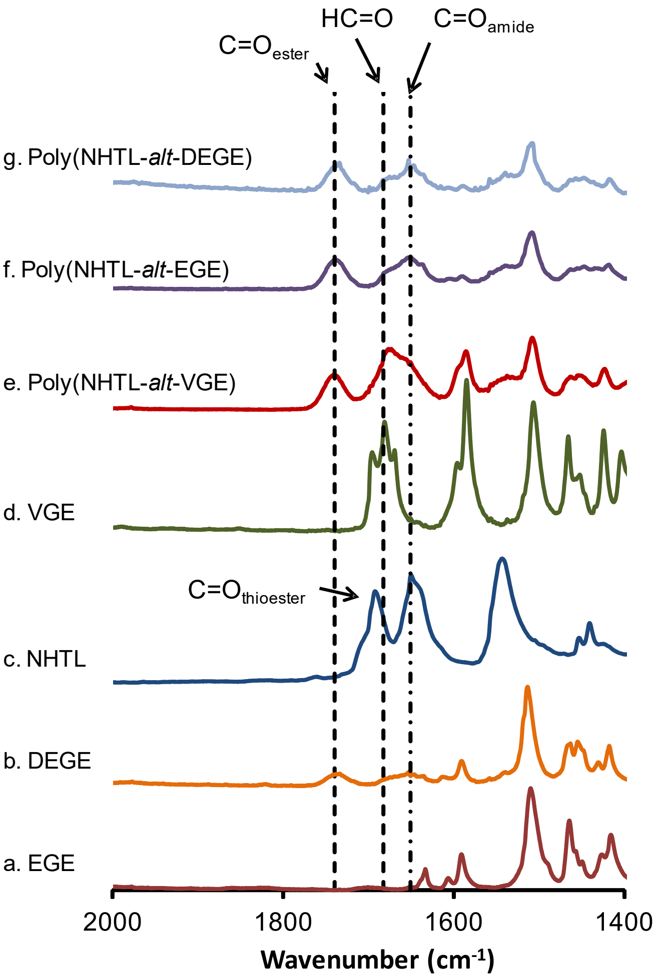


Figure S15. ATR-FTIR analysis of: a) EGE; b) DEGE; c) NHTL; d) VGE; e) Poly(NHTL-*alt*-VGE) (Table 1, run 23); f) Poly(NHTL-*alt*-EGE) (Table 1, run 10); g) poly(NHTL-*alt*-DEGE) (Table 1, run 6).

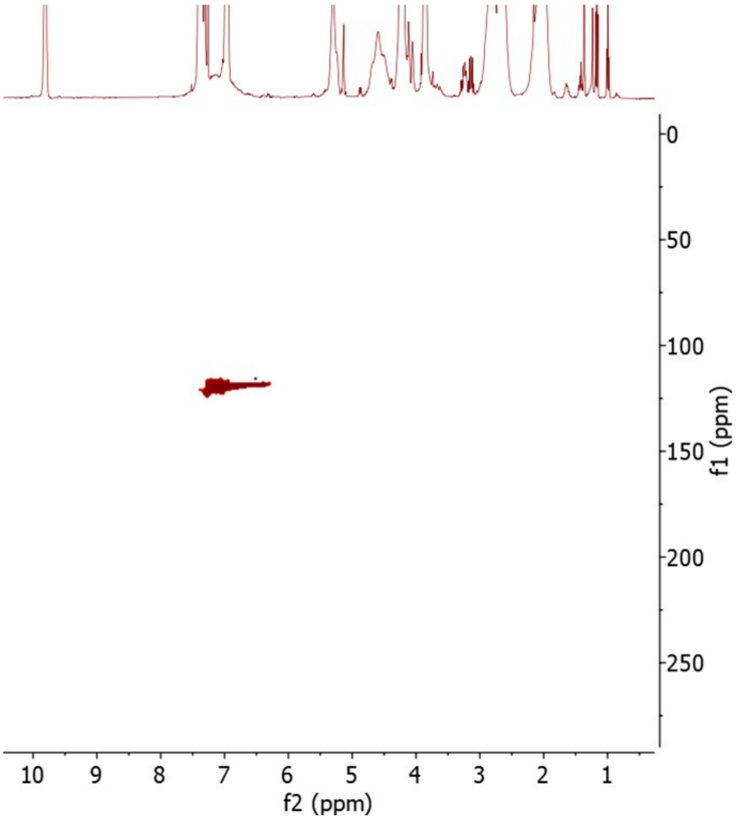


Figure S16. 2D ^{1}H-^{15}N HSQC NMR spectrum in acetone-d_6 at 25 °C of poly(NHTL-*alt*-VGE) (Table 1, run 24).

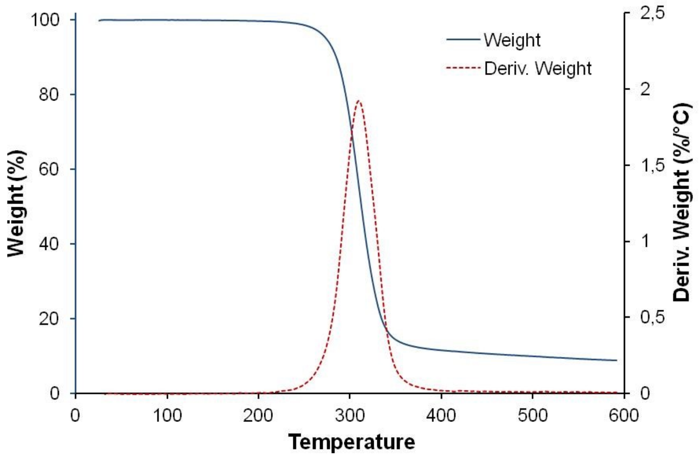


Figure S17. TGA curve and its first derivative measured under a stream of nitrogen between 20°C and 600°C with a heating rate of 20 °C.min^{-1} for a poly(NHTL-*alt*-DEGE) (Table 1, run 6).

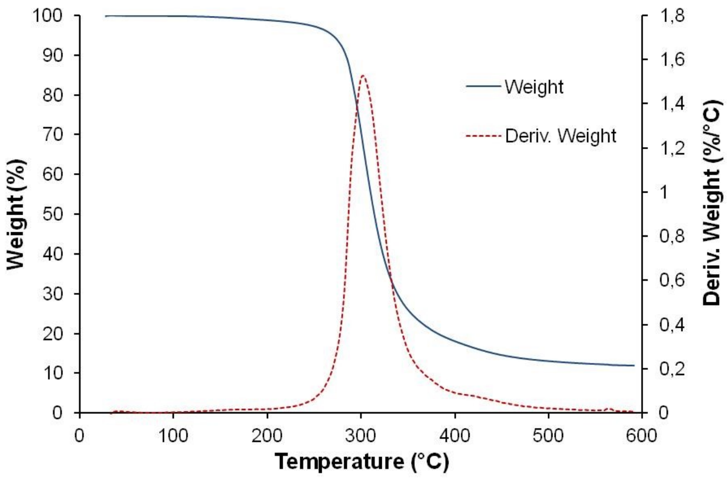


Figure S18. TGA curve and its first derivative measured under a stream of nitrogen between 20°C and 600°C with a heating rate of 20 °C.min^{-1} for a poly(NHTL-*alt*-EGE) (Table 1, run 10).

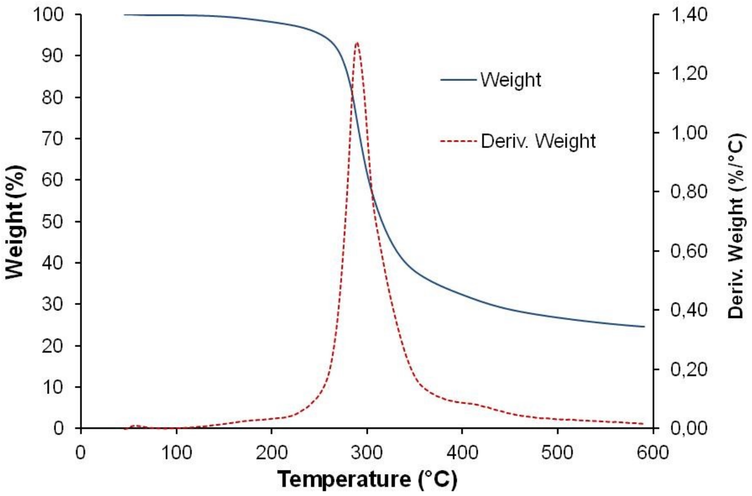


Figure S19. TGA curve and its first derivative measured under a stream of nitrogen between 20°C and 600°C with a heating rate of 20 °C.min^{-1} for a poly(NHTL-*alt*-VGE) (Table 1, run 24).

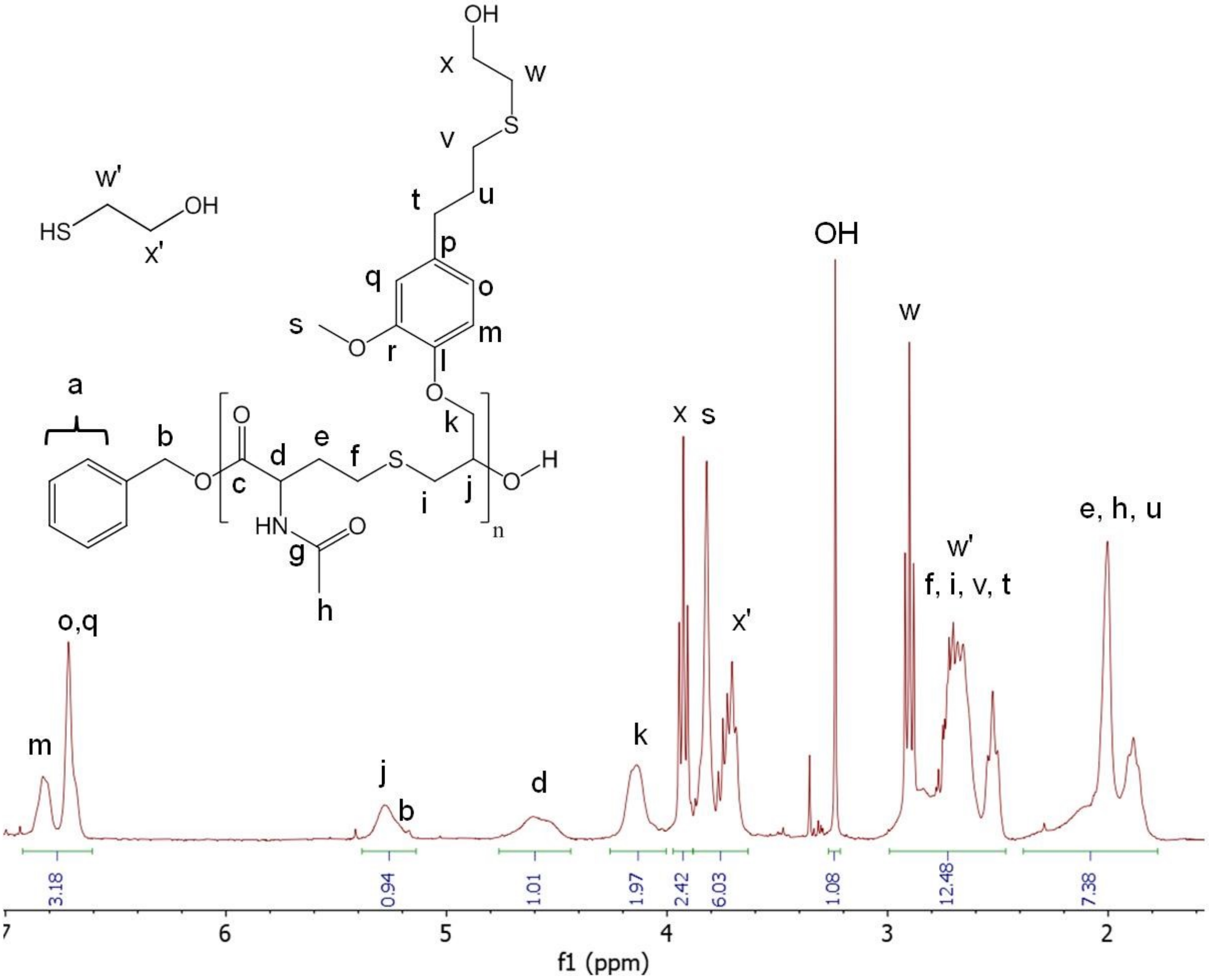


Figure S20. ^{1}H NMR spectrum in $CDCl_3$ at 25°C of a poly(NHTL-*alt*-EGE) (Table 1, run 15) modified by thiol-ene addition with 2-mercaptoethanol.