Electronic Supplementary Material (ESI) for Polymer Chemistry.

Epoxy-functionalised 4-vinylguaiacol for the synthesis of bio-based, degradable star polymers *via* a RAFT/ROCOP strategy

Contents

1. Materials and Methods

Materials. 4-Vinylguaiacol (4VG)[1] and cumyl dithiobenzoate (CDB)[2] were synthesised according to literature methods. Styrene (St, Kishida, 99.5%), dethylacrylamide (DEAA, Tokyo Chemical Industry, >98%), *o*-dichlorobenzene (Tokyo Chemical Industry, >99%), 1,2,3,4-tetrahydronaphthalene (Wako, 97%) were purified by distillation over CaH_2. Toluene (KANTO, >99.5%; H_2O <0.001%), was dried and deoxygenized by passage through columns of Glass Contour Solvent Systems before use. *cis*-4-Cyclohexene-1,2-dicarboxylic anhydride (CDCA, Tokyo Chemical Industry, >98%) was singly recrystallised from anhydrous toluene. Bis(triphenylphosphine)iminium chloride (PPNCl, Aldrich, 97%) was singly recrystallised from anhydrous acetonitrile. α,α-Azobisisobutyronitrile (AIBN, Kishida, >99%) was purified by recrystallisation from methanol. Ferulic acid (Aldrich, >99%), dimethylformamide (Alfa-aesar, >99.5%), triethylamine (Aldrich, >99%), epichlorohydrin (Acros organics, 99%), benzyltriethylammonium chloride (Aldrich, 99%), *N*,*N'*-Dicyclohexylurea (Aldrich, 98%), (*R,R*)-*N,N'*-Bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediaminochromium(III) chloride (Aldrich) were used as received.

^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker 400, 500 or JEOL ECS 400 MHz instrument and referenced to residual solvent peaks. Coupling constants are given in Hertz. Details for conversion calculations are given in the general procedures.

Size exclusion chromatography (SEC) was used to calculate the number-average molecular weight (M_n) and the molecular weight distribution (M_w/M_n) of the polymers in THF eluent at 40 °C on two polystyrene gel columns [TSKgel MultiporeHXL-M (7.8 mm i.d. × 30 cm)] connected to a JASCO PU-2080 precision pump and a JASCO RI-2031 detector. The columns were calibrated against 10 polystyrene (Varian; M_p = 580–3,242,000 Da, M_w/M_n = 1.02–1.23) or polymethylmethacrylate (Agilent Technologies; M_p 202–1,677,000, M_w/M_n = 1.02–1.23) standard. .

Multi angle light scattering (MALLS) analysis was performed in THF on a Dawn HELEOS photometer (Wyatt Technology; 1–633 nm). The refractive index increments were measured in THF at 40 °C on an Optilab rEX (Wyatt Technology; 1–633 nm).

Differential scanning calorimetry (DSC) was recorded using a Q200, TA instrument (USA). Samples of 2 – 5 mg were placed in aluminium pans and sealed, and measurements were carried out between−50 and 300 °C with a heating rate of 10°C/min and a cooling rate of 5°C/min under nitrogen flow. The glass transitions (T_g) were taken as the mid-point of the change in heat capacity during the second heating run. Data was plotted using Origin 2018 software.

Thermogravimetric analysis (TGA) was recorded using a Q500, TA instrument (USA). Samples of 2 – 5 mg were placed in aluminium pans and sealed. Samples were first equilibrated at 110 °C for 30 minutes, then equilibrated at 40 °C before heating at 5 °C/min to 500 °C. Data was plotted using Origin 2018 software.

2. General Procedures

2.1 Synthesis of 2-((2-methoxy-4-vinylphenoxy)methyl)oxirane, 4VGEP

4VGEP was synthesised following a modified literature procedure:[3] a vessel was charged with 4-vinyl guaiacol (5.0 g, 33.3 mmol), epichlorohydrin (10.5 ml, 133.2 mmol, 4 equiv.) and benzyltriethyl ammonium chloride (0.758 g, 3.33 mmol, 0.1 equiv.) The resultant off-white suspension was heated to 100 °C. After 90 minutes, sodium hydroxide (22 mL of a 2000 mM solution, 66.6mmol, 2 equiv.) and a second batch of benzyltriethyl ammonium chloride (0.758 g, 3.33 mmol, 0.1 equiv.) were added to the vessel. The reaction was left to stir at room temperature for a further 90 minutes. The mixture was then extracted into ethyl acetate (150 ml) and washed with brine (50 ml, times 2) and water (50 ml, times 1). The organic phase was collected, dried over magnesium sulphate and the solution concentrated under reduced pressure. Purification by column chromatography (diameter of column = 7.6 cm, mass of silica = 275 g, 7:3 petroleum ether:ethyl acetate) followed by recrystallization in hexane affords 4VGEP as a white solid in 82% yield (5.6 g); $\mathbf{R}_f$ 0.25 (3:7 petroleum ether: ethyl acetate);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.00 – 6.82 (m, 3H, $\mathbf{H}_c$), 6.64 (dd, *J* = 17.6, 10.8 Hz, 1H, $\mathbf{H}_b$), 5.62 (dd, *J* = 17.6, 0.9 Hz, 1H, $\mathbf{H}_a$), 5.15 (dd, *J* = 10.8, 0.9 Hz, 1H, $\mathbf{H}_a$), 4.23 (dd, *J* = 11.4, 3.5 Hz, 1H, $\mathbf{H}_d$), 4.02 (dd, *J* = 11.4, 5.6 Hz, 1H, $\mathbf{H}_e$), 3.88 (s, 3H, $\mathbf{H}_d$), 3.37 (ddt, *J* = 6.0, 3.8, 1.9 Hz, 1H, $\mathbf{H}_f$), 2.88 (dd, *J* = 4.9, 4.1 Hz, 1H, $\mathbf{H}_g$), 2.73 (dd, *J* = 4.9, 2.6 Hz, 1H, $\mathbf{H}_f$).

^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 149.7 ($\mathbf{Ar}_c$), 148.0 ($\mathbf{Ar}_c$), 136.4 ($\mathbf{C}_b$), 131.8 ($\mathbf{Ar}_c$), 119.4 ($\mathbf{Ar}_c$), 114.0 ($\mathbf{Ar}_c$), 112.3 ($\mathbf{C}_a$) , 109.4 ($\mathbf{Ar}_c$), 70.3 ($\mathbf{C}_e$), 55.9 ($\mathbf{C}_d$), 50.2 ($\mathbf{C}_f$) , 44.9 ($\mathbf{C}_g$).

HR-MS (ESI): [$C_{12}H_{14}O_3$+Na]$^+$ Theo. 229.0838, found 229.0835. Atom economy of the procedure: 32%. E-factor: 66.

2.2 Polymerisation procedures

2.21 RAFT polymerisation of 4VGEP

RAFT polymerisation was carried out by syringe technique under dry nitrogen in sealed glass tubes. A typical example for polymerisation of 4VGEP with CDB as the RAFT agent in the presence of AIBN is given below:

4VGEP (2.000 g, 9.69 mmol, 100 equiv.), CDB (0.026 g, 0.0969 mmol, 1 equiv.), AIBN (0.24 mL of 0.1 mol L^{-1} solution in toluene, 0.024 mmol, 0.25 equiv.), 1,2,3,4-tetrahydronaphthalene (0.10 mL) as an internal standard and toluene were added to a 25 mL round-bottomed flask equipped with a three-way stopcock. The total volume of the reaction mixture was 3.2 mL. The mixture was heated to 60 °C until fully dissolved. Immediately after dissolution, the solution was evenly charged to six glass tubes, and the tubes sealed by flame under a nitrogen atmosphere. The tubes were heated to 60 °C. At predetermined intervals, the polymerisation was terminated by cooling the reaction mixtures to –78 °C. Monomer conversion was determined from the concentration of residual monomer measured by ^{1}H NMR spectroscopy using the peak intensity ratio between the monomer/polymer resonances at 2.69–2.95 ppm and monomer resonances at 5.17 ppm. The quenched reaction solutions were evaporated to dryness to give P4VGEP ($M_{\mathrm{n,SEC}}$ = 6900, $Đ_{\mathrm{M,SEC}}$ = 1.07).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 (b, $\mathbf{H}_x$), 6.57 (b, $\mathbf{H}_c$), 6.01 (b, $\mathbf{H}_c$), 4.14 (b, $\mathbf{H}_e$), 3.90 (b, $\mathbf{H}_e$), 3.58 (b, $\mathbf{H}_d$),3.31 (b, $\mathbf{H}_f$), 2.84 (b, $\mathbf{H}_g$), 2.70 (b, $\mathbf{H}_g$), 2.20 – 1.16 (b, $\mathbf{H}_a$, $\mathbf{H}_b$).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.1 (b, $\mathbf{Ar}_c$), 146.0 ($\mathbf{Ar}_c$), 139.2 (b, $\mathbf{Ar}_c$), 119.5 (b, $\mathbf{Ar}_c$), 113.8 (b, $\mathbf{Ar}_c$),111.5 ($\mathbf{Ar}_b$), 70.4 ($\mathbf{C}_e$), 55.8 ($\mathbf{C}_d$), 50.3 ($\mathbf{C}_f$), 44.7 ($\mathbf{C}_g$), 40.3 (b, $\mathbf{C}_a$, $\mathbf{C}_b$).

2.22 Synthesis of block copolymers.

A typical example for the synthesis of St-*b*-4VGEP block copolymer is given below:

The RAFT polymerisation of styrene was carried out in a 50 mL round-bottomed flask equipped with a three-way stopcock containing styrene (20.00 mL, 173.98 mmol, 200 equiv.) and CDB (0.236 g, 0.87 mmol, 1 equiv.) giving a total volume of 20.2 mL. The reaction mixture was heated to 110 °C. After 11 h, the polymerisation was terminated by cooling the reaction mixtures to –78 °C. Monomer conversion was determined from the concentration of residual monomer measured by ^{1}H NMR using the peak intensity ratio between the monomer/polymer resonances at 6.40–7.61 ppm and the monomer resonances at 5.30 ppm. The quenched reaction mixture was evaporated to dryness. The obtained polymer was purified by re-precipitation of 10wt% $HCCl_3$ solution of polymer in methanol at room temperature to give PSt ($M_{\mathrm{n,SEC}}$ = 9800, $Đ_{\mathrm{M}}$ = 1.08).

The obtained PSt was employed as the macro-RAFT agent for the block copolymerisation with 4VGEP. 4VGEP (2.000 g, 9.70 mmol, 50 equiv.) and PSt (2.268 g, 0.19 mmol,1 equiv.) were charged to a 25 mL round bottom flask equipped with a three-way stopcock and dissolved in toluene (0.70 ml). The total volume of the reaction mixture was 5.0 mL. The reaction mixture was heated to 110 °C. After 220 minutes, the polymerisation was terminated by cooling the reaction mixture to –78 °C. Monomer conversion was determined from the concentration of residual monomer measured by ^{1}H NMR using peak intensity ratio between the monomer/polymer resonances at 2.69–2.95 ppm and monomer resonances at 5.17 ppm. The quenched reaction solutions were evaporated to dryness and the polymer reprecipitated as a 10 wt% $HCCl_3$ solution in methanol to give St-*b*-4VGEP (M_{n} = 11700, $Đ_{\mathrm{M}}$ = 1.08).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 (b, **H**$_x$), 7.04 (b, **H**$_c$), 6.58 (b, **H**$_f$), 4.15 *(b,* **H**$_h$) 3.93 (b, **H**$_h$), 3.57 (b, **H**$_g$), 3.33 (b, **H**$_i$), 2.84 (b, **H**$_j$), 2.72 (b, **H**$_j$), 1.85 (b, **H**$_b$**,** **H**$_e$), 1.44 (b, **H**$_a$**,** **H**$_d$).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 148.1 (b, **Ar**$_f$), 144.3 (b, **Ar**$_c$), 127.0 (b, **Ar**$_c$), 124.6(b, **Ar**$_c$), 118.3 (b, **Ar**$_f$), 112.4 (b, **Ar**$_f$), 69.31 (**C**$_e$), 54.73 (**C**$_g$), 49.25 (**C**$_i$), 46.2 – 36.6 (b, **C**$_a$, **C**$_b$, **C**$_d$, **C**$_e$ **,C**$_j$).

For DEAA-*b*-4VGEP: as above, characterisation: ($M_{\mathrm{n,SEC}}$ = 18500, $Đ_{\mathrm{M}}$ = 1.10).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 (*b*, **H**$_x$), 6.55 (*b*, **H**$_g$), 5.98 (*b*, **H**$_g$), 4.16 (*b*, **H**$_i$), 3.87 (*b*, **H**$_i$), 3.43 (*b*, **H**$_c$**,** **H**$_h$**,** **H**$_j$), 2.85 (*b*, **H**$_k$), 2.60 (*b*, **H**$_b$), 1.67 (*b*, **H**$_a$, **H**$_f$), 1.03 (*b*, **H**$_d$**,** **H**$_e$).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 173.8 (C=O), 149.4 (b, **Ar**$_g$), 146.0(**Ar**$_g$), 139.7 (b, **Ar**$_g$), 119.7 (b, **Ar**$_g$), 113.7 (b, **Ar**$_g$), 70.4 (**C**$_i$), 55.9 (**C**$_h$), 50.4 (**C**$_j$), 44.9 (b, **C**$_k$), 43.1 – 33.8 (b*,* **C**$_a$**,** **C**$_b$**,** **C**$_e$**,** **C**$_f$), 14.6 (**C**$_c$), 13.1 (**C**$_d$),.

2.23 Synthesis of star polymers.

A typical example for the synthesis of *Star* St-*b*-4VGEP star polymer is given below:

Block copolymer, St-*b*-4VGEP (0.200 g, 0.0170 mmol, 1 equiv.) and CDCA (0.035 g, 0.238 mmol, 14 equiv.) were charged to a 25 mL round-bottomed flask equipped with a three-way stopcock and dissolved in *o*-dichlorobenzene (0.16 mL). *N*,*N'*-Dicyclohexylurea (9.52×10^{-3} mmol, 0.56 equiv) and PPNCl (9.52×10^{-3} mmol, 0.56 equiv) were added to the reaction mixture from an equimolar stock solution (0.10 mL of a 9.52×10^{-1} mol L^{-1} stock solution). The total volume of the reaction mixture was 0.5 mL. The reaction mixture was heated to 110 °C. Monomer conversion was determined from the concentration of residual monomer measured by ^{1}H NMR using peak intensity ratio between the solvent resonances at 7.44 ppm and the anhydride monomer resonances at 2.62 ppm. After 3 h, the polymerisation was terminated by quenching with 1.0M HCl. The polymer solution was diluted with chloroform and washed with 1.0 M HCl followed by water. The solution was concentrated under reduced pressure and the polymer isolated by preparative GPC to afford *star*-St-*b*-4VGEP ($M_{\mathrm{n,SEC}}$ = 102800, $Đ_{\mathrm{M,\,SEC}}$ = 1.25, $M_{\mathrm{n,MALLS}}$ = 156100, f_{arm} = 13.4).

2.3 Degradation procedure

2.3.1 Degradation of *star*-St-b-4VGEP

Star polymer, *star*-St-*b*-4VGEP (0.020 g), 20% aqueous trifluoroacetic anhydride (1 mL) and toluene (1 mL) were charged to a round-bottomed flask forming a pink suspension. The reaction mixture was heated to 100 °C with slow dissolution of the solid to form a red/brown solution. At predetermined intervals, aliquots were taken, and the degradation monitored by SEC.

3. Characterisation

3.1 SEC traces

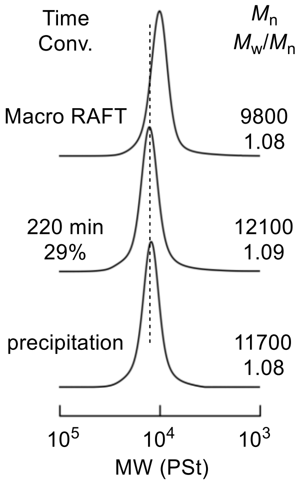


Fig. S1. M_n, $Đ_M$, and SEC curves of St-*b*-4VGEP obtained in the RAFT copolymerisation at loadings of $[4VGEP]_0$:$[PS]_0$ of 50:1 in *o*-dichlorobenzene at 110 °C. $[4VGEP]_0$ = 2.0 mol L^{-1}

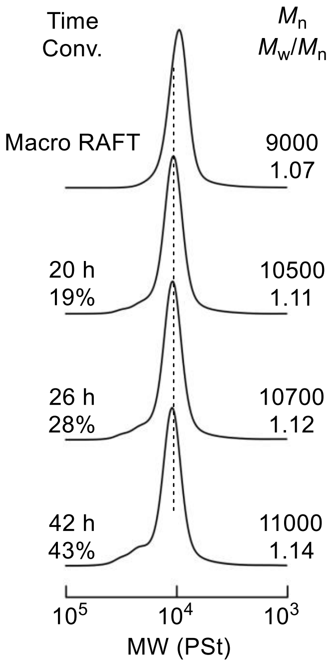


Fig. S2. M_n, $Đ_M$, and SEC curves of St-*b*-4VGEP obtained in the RAFT copolymerisation at loadings of $[4VGEP]_0$:$[PS]_0$:$[AIBN]_0$ of 20:1:0.2 in toluene at 60 °C. $[4VGEP]_0$ = 0.75 mol L^{-1}

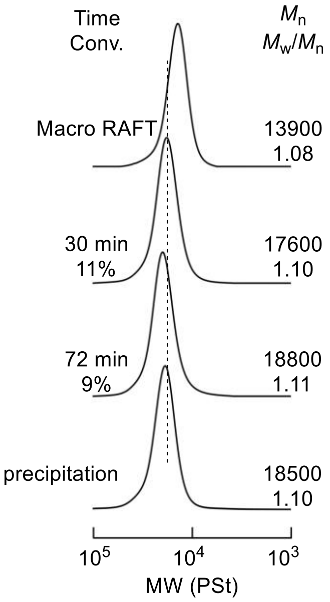
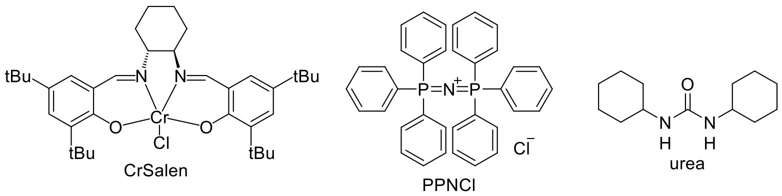


Fig. S3. M_n, $Đ_M$, and SEC curves of DEAA-*b*-4VGEP obtained in the RAFT copolymerisation at loadings of $[4VGEP]_0$:$[PDEAA]_0$ of 100:1 in *o*-dichlorobenzene at 110 °C. $[4VGEP]_0 = 2.0$ mol L^{-1}



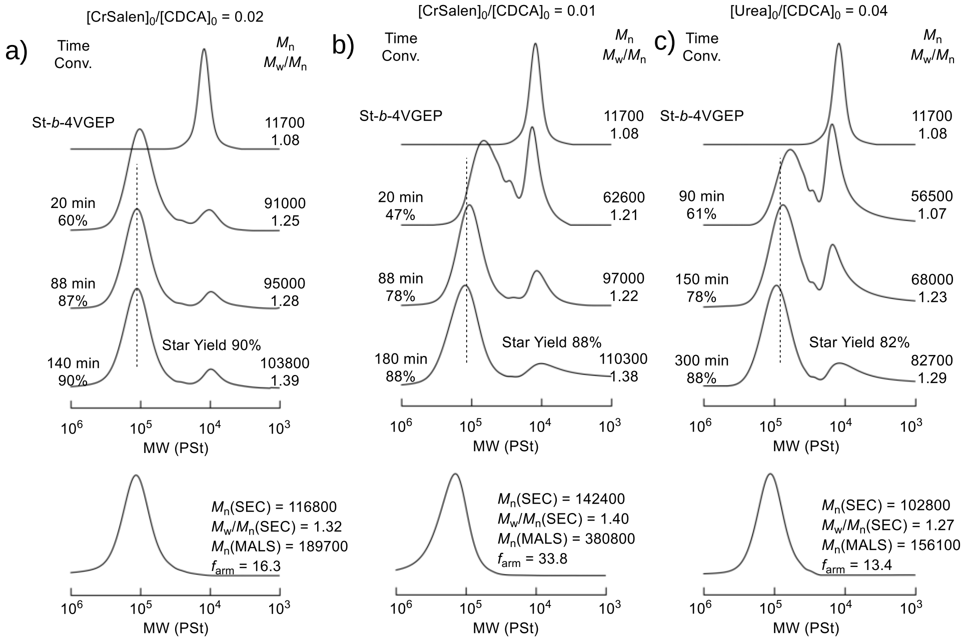


Fig. S4. M_n, $Đ_M$, and SEC curves of *star*-St-*b*-4VGEP obtained in the epoxide/anhydride copolymerisation in *o*-dichlorobenzene at 110 °C at loadings of: a) [St-*b*-4VGEP]$_0$:[CDCA]$_0$:[CrSalen]$_0$:[PPNCl]$_0$ of 10:140:2.8:2.8 b) [St-*b*-4VGEP]$_0$:[CDCA]$_0$:[CrSalen]$_0$:[PPNCl]$_0$ of 10:140:1.4:1.4 c). [St-*b*-4VGEP]$_0$:[CDCA]$_0$:[urea]$_0$:[PPNCl]$_0$ of 10:140:5.6:5.6

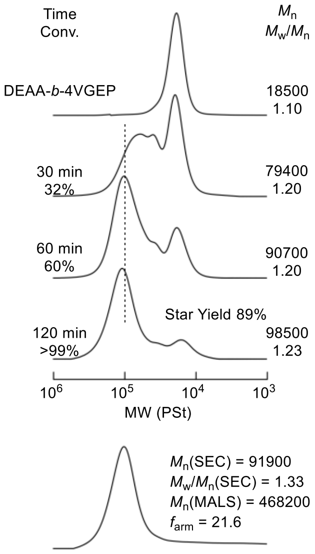


Fig. S5 M_n, $Đ_M$, and SEC curves of *star*-DEAA-*b*-4VGEP obtained in the epoxide/anhydride copolymerisation in *o*-dichlorobenzene at 110 °C at loadings of [DEAA-*b*-4VGEP]$_0$:[CDCA]$_0$:[urea]$_0$:[PPNCl]$_0$ of 10:170:6.8:6.8

3.2 NMR characterisation

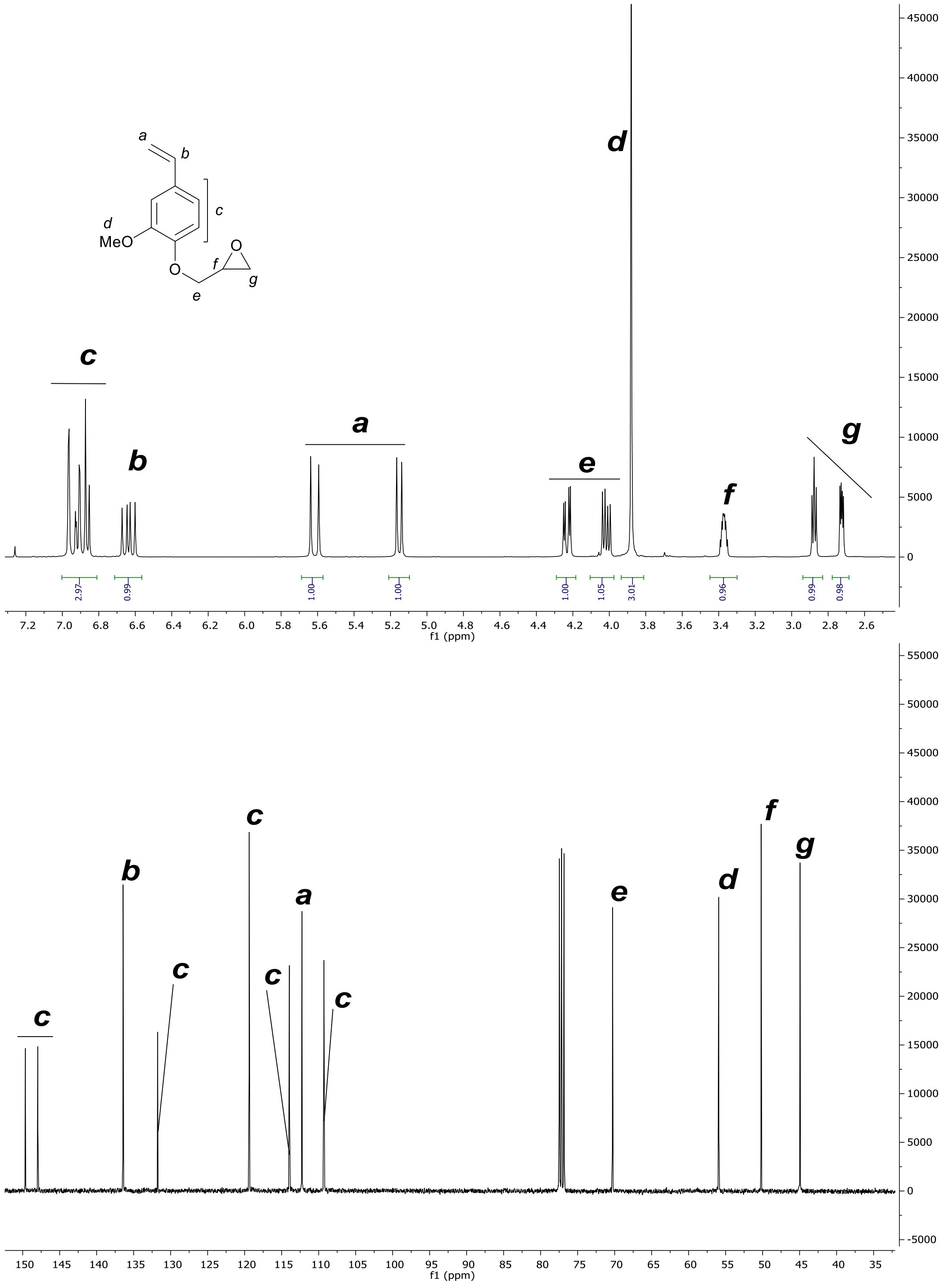


Fig. S6. (top) ^{1}H NMR spectrum of 4VGEP ($CHCl_3$ residual signal at 7.26 ppm) (bottom): ^{13}C NMR spectrum of 4VGEP ($CHCl_3$ residual signal at 77.2 ppm)

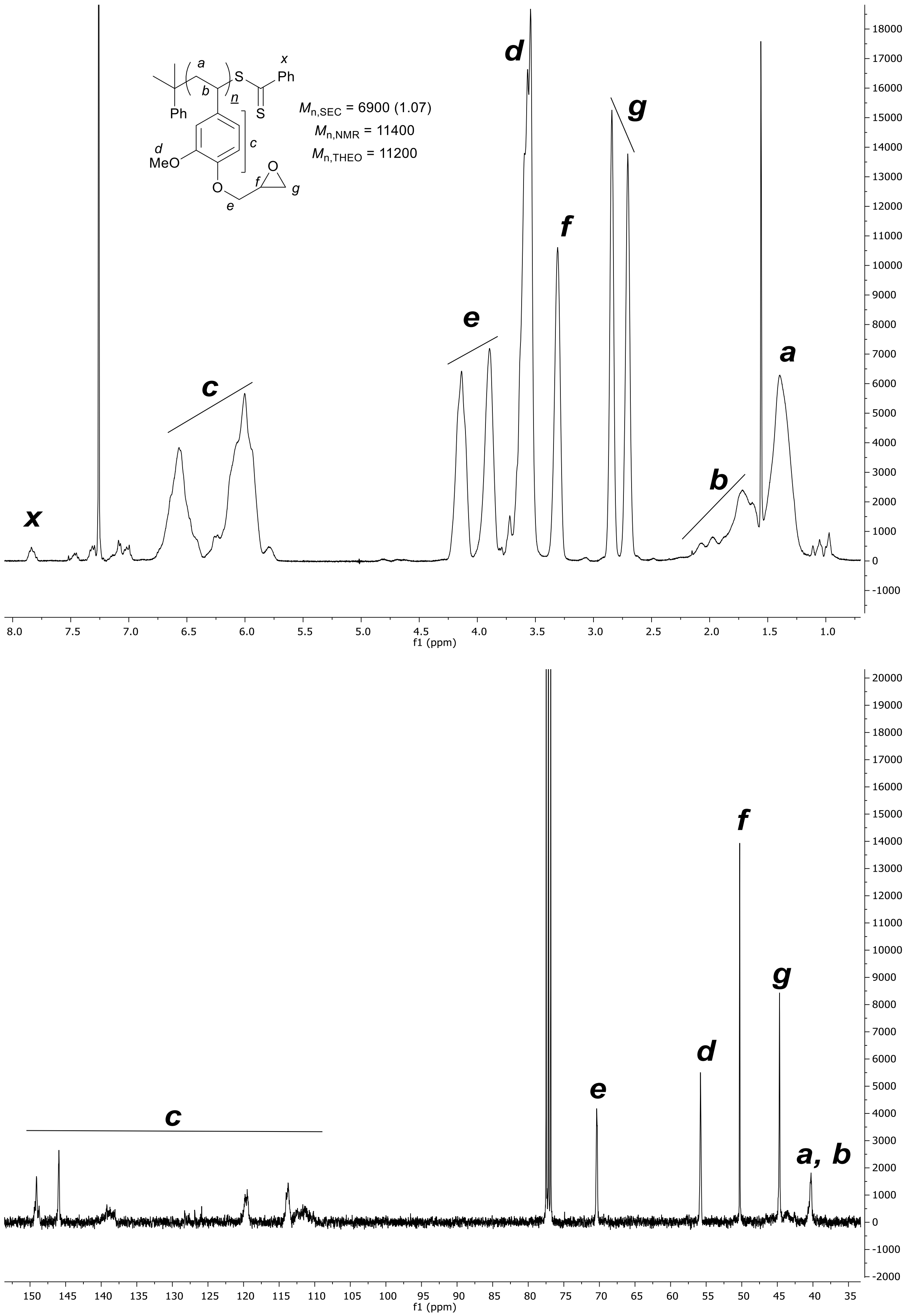


Fig. S7. (top) ^{1}H NMR spectrum of P4VGEP ($CHCl_3$ residual signal at 7.26 ppm, H_2O residual signal at 1.51) (bottom): ^{13}C NMR spectrum of P4VGEP ($CHCl_3$ residual signal at 77.2 ppm)

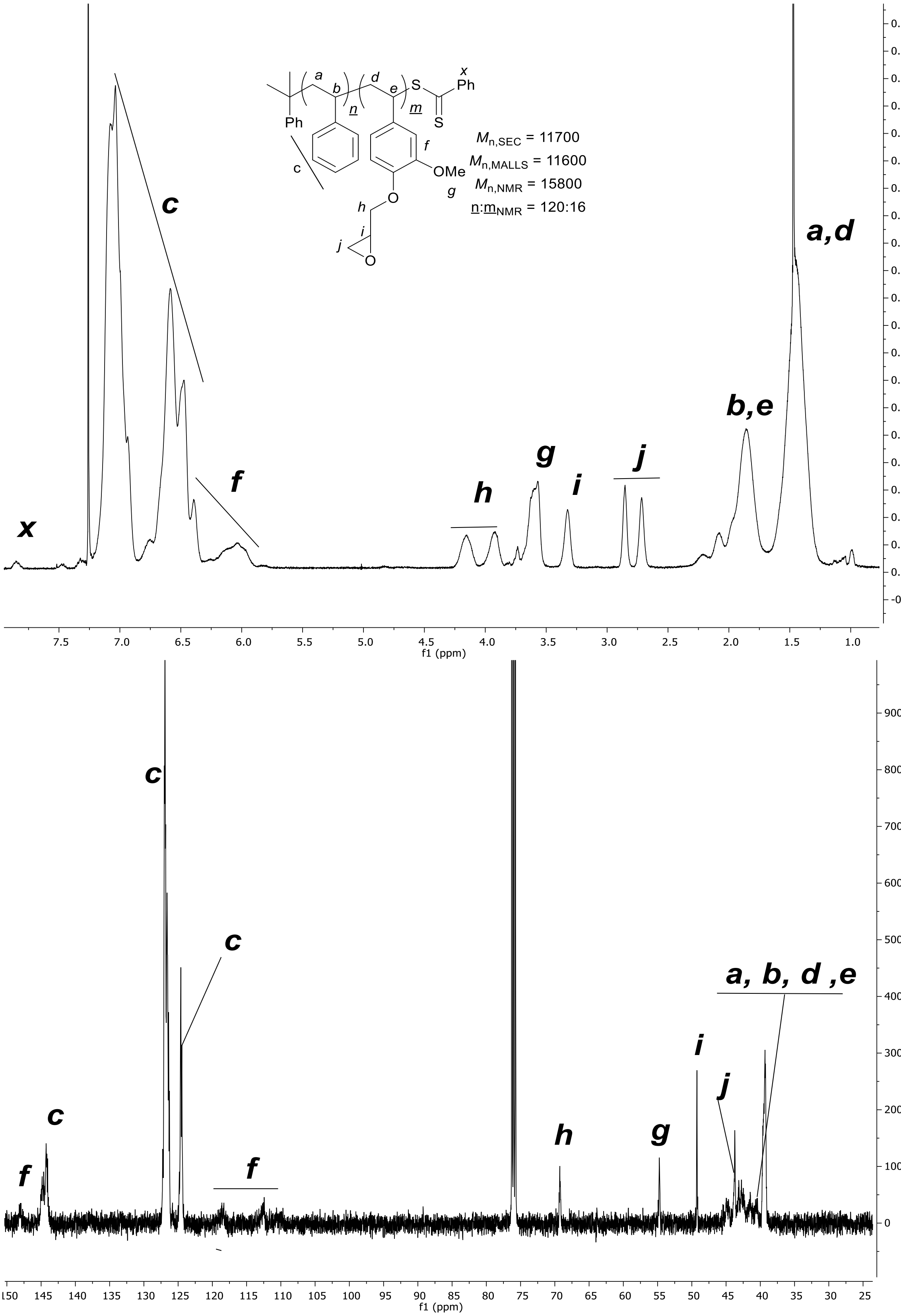


Fig. S8. (top): ^{1}H NMR spectrum of St-*b*-P4VGEP ($CHCl_3$ residual signal at 7.26 ppm, H_2O residual signal at 1.51) (bottom): ^{13}C NMR spectrum of St-*b*-P4VGEP ($CHCl_3$ residual signal at 77.2 ppm)

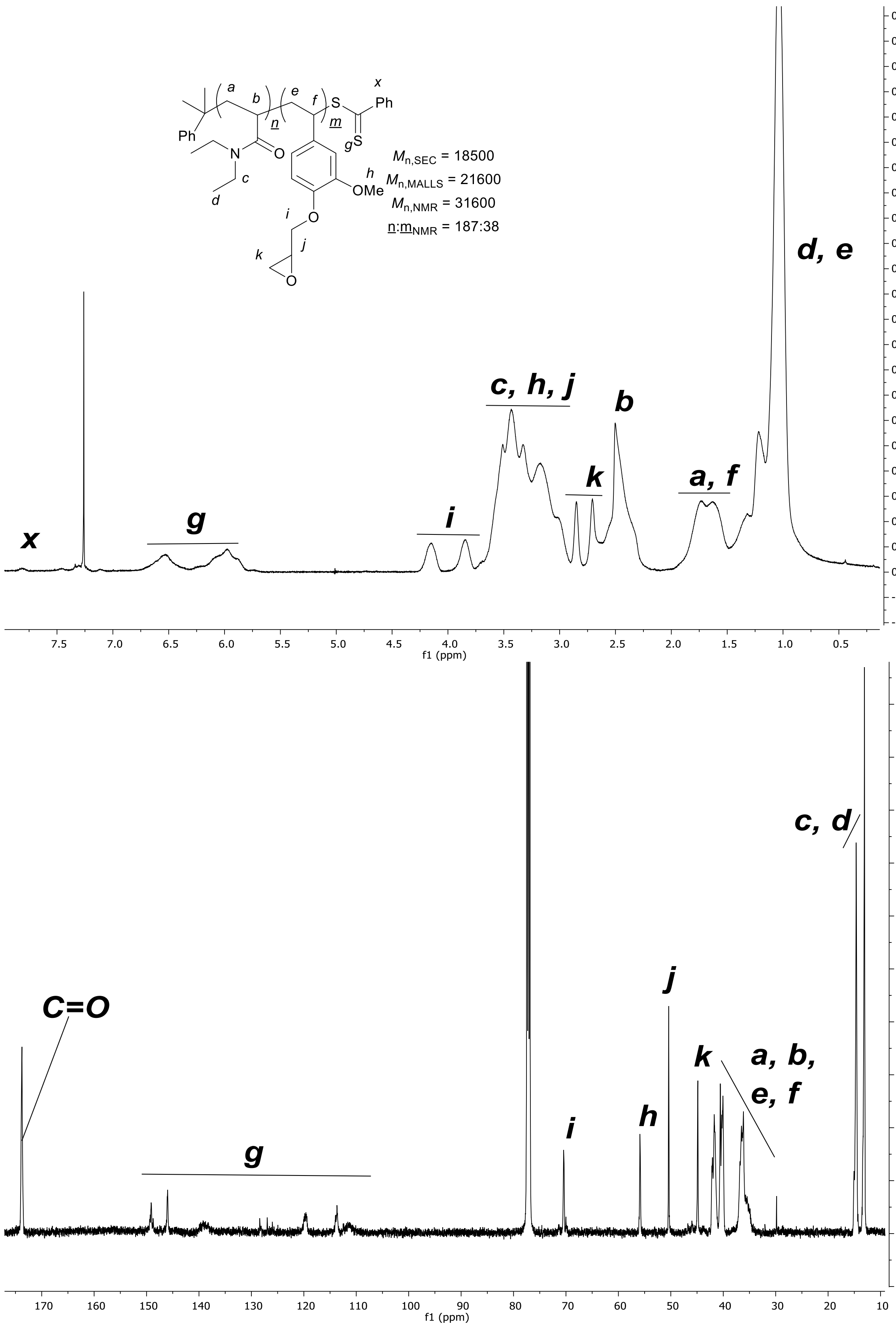


Fig. S9. (top) ^{1}H NMR spectrum of DEAA-*b*-P4VGEP (CHCl$_3$ residual signal at 7.26 ppm) (bottom): ^{13}C NMR spectrum of DEAA-*b*-P4VGEP (CHCl$_3$ residual signal at 77.2 ppm)

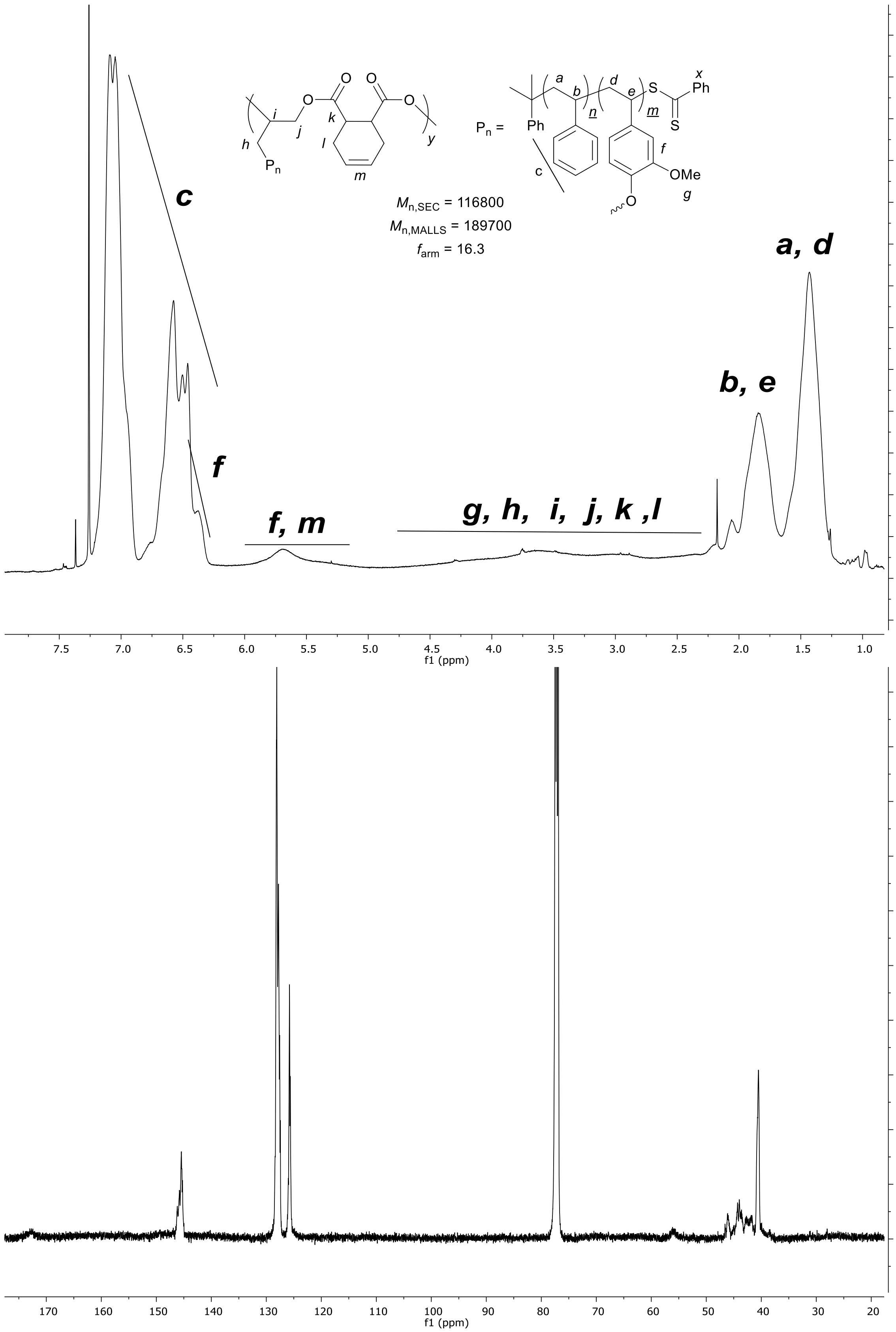


Fig. S10. (top) ^{1}H NMR spectrum of *Star*-St-*b*-P4VGEP ($CHCl_3$ residual signal at 7.26 ppm, acetone residual signal at 2.17) (bottom): ^{13}C NMR spectrum of St-*b*-P4VGEP ($CHCl_3$ residual signal at 77.2 ppm)

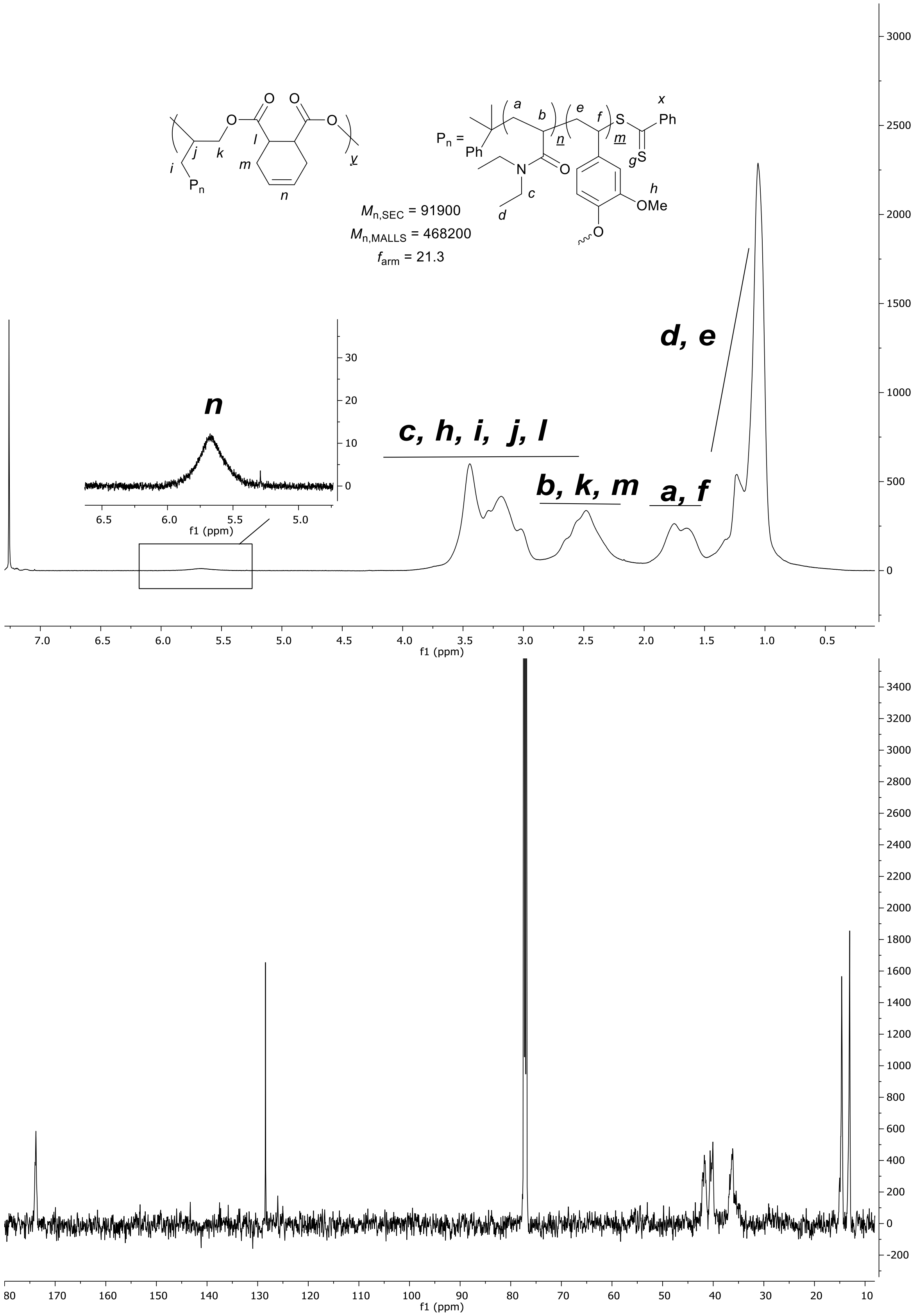


Fig. S11. (top) ^{1}H NMR spectrum of *Star*-DEAA-*b*-P4VGEP ($CHCl_3$ residual signal at 7.26 ppm) (bottom): ^{13}C NMR spectrum of *Star*-DEAA-*b*-P4VGEP ($CHCl_3$ residual signal at 77.2 ppm, C_6H_6 residual signal at 128.4 ppm)

3.3 Thermal characterisation

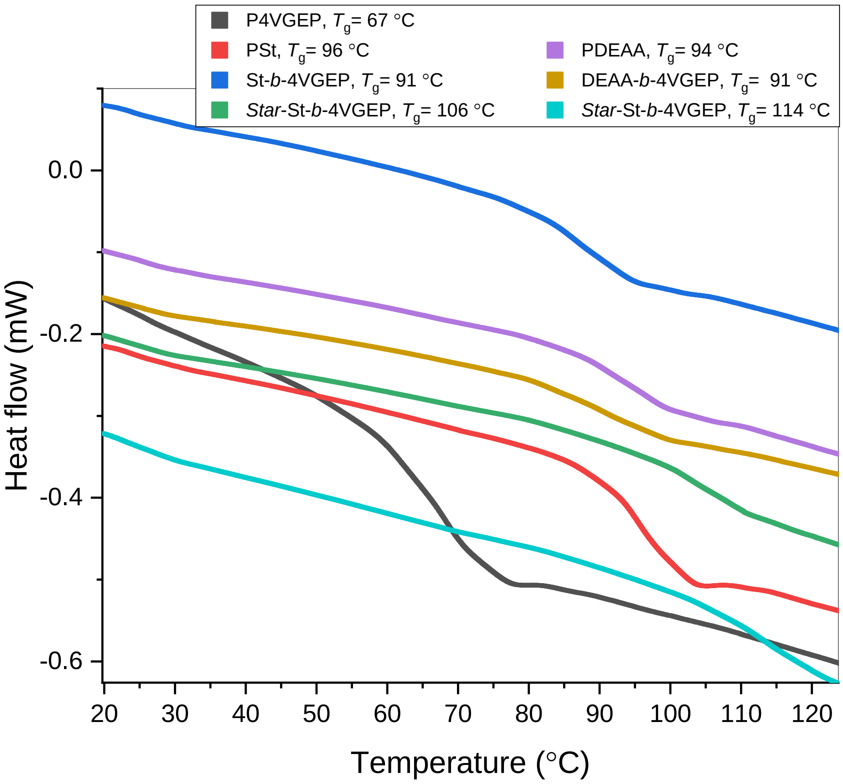


Fig. S12. DSC thermograms of all polymers isolated in this study: P4VGEP (dark grey, $M_{n,SEC}$ = 6900), PSt (red, $M_{n,SEC}$ = 9800), St-*b*-4VGEP (blue, $M_{n,SEC}$ = 11700), *star*-St-*b*-4VGEP (green, $M_{n,SEC}$ =116800), PDEAA (lilac, $M_{n,SEC}$ = 13900), DEAA-*b*-4VGEP (gold, $M_{n,SEC}$= 18500) and *star*-DEAA-*b*-4VGEP (cyan, $M_{n,sec}$ = 107700)

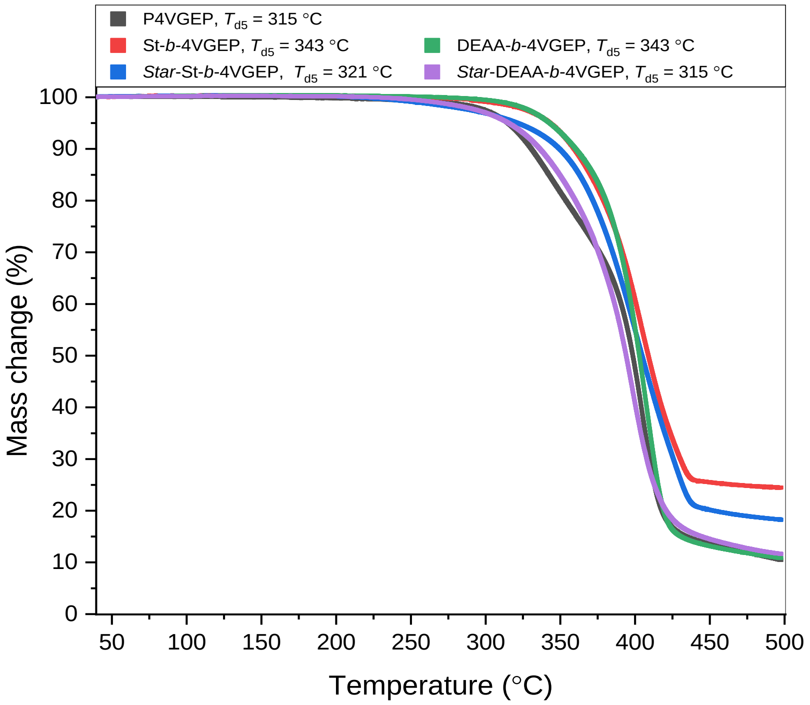


Fig. S13. TGA traces of all novel polymers isolated in this study: P4VGEP (dark grey, $M_{n,SEC}$ = 6900), St-*b*-4VGEP (red, $M_{n,SEC}$ = 11700), *star*-St-*b*-4VGEP (blue, $M_{n,SEC}$ =116800), DEAA-*b*-4VGEP (green, $M_{n,SEC}$= 18500) and *star*-DEAA-*b*-4VGEP (lilac, $M_{n,sec}$ = 107700)

4. Hydrolytic degradation of *star*-St-*b*-4VGEP

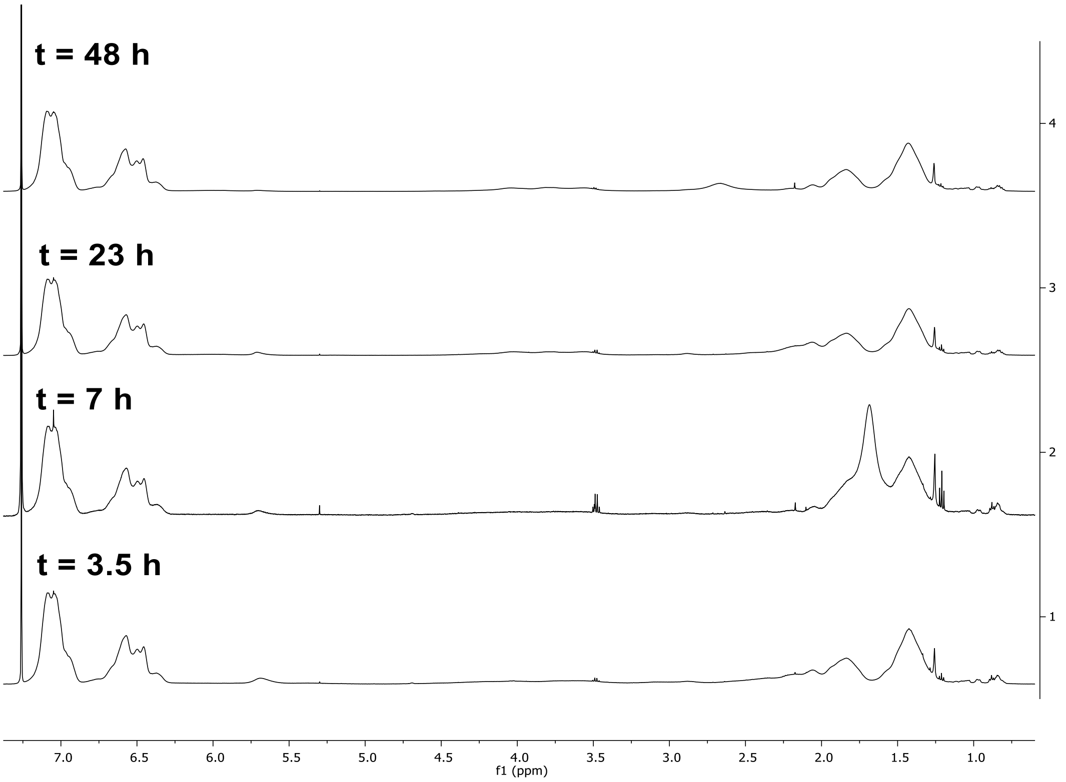


Fig. S14. ^{1}H NMR spectra of samples taken during the acid hydrolysis of *star*-St-*b*-4VGEP **(**$CHCl_3$ residual signal at 7.26 ppm, Et_2O residual signals at 1.21 ppm and 3.47 ppm).

5. References

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2. Moad, G.; Chiefari, J.; Chong, Y. K.; Krstina, J.; Mayadunne, R. T. A.; Postma, A.; Rizzardo, E.; Thang, S. H. *Polym. Int*., 2000, **49**, 993–1001.
3. E. Zago, E. Dubreucq, J. Lecomte, P. Villeneuve, F. Fine, H. Fulcrand and C. Aouf, *New J. Chem.*, 2016, **40**, 7701-7710.