Geometry-directed cyclisation within the transfer-dominated branching radical telomerisation of dimethacrylates.

Corinna Smith[a,b], Oliver B. Penrhyn-Lowe[a,b], Samuel Mckeating[a,b], Stephen Wright[a,b], Andrew B. Dwyer[a,b], and Steve P. Rannard*[a,b]

[a]   Department of Chemistry, University of Liverpool, Crown Street, Liverpool, L69 7ZD, UK

[b]   Materials Innovation Factory, University of Liverpool, 51 Oxford Street, Liverpool, L7 3NY, UK

[*]   Corresponding author E-mail: srannard@liv.ac.uk

Experimental

Materials

2,2'azobis(isobutyronitrile) (AIBN, 98 %), 1-Dodecanethiol (DDT, 98 %), ethylene glycol dimethacrylate (EGDMA 98 %) and $CDCl_3$ (99.8 atom% D) were purchased from Sigma Aldrich. Ethyl acetate (EtOAc, analytical grade), methanol (MeOH, analytical grade 99.9 %), tetrahydrofuran (THF, HPLC-grade) and toluene (reagent grade) were purchased from Fisher. Neopentyl glycol dimethacrylate (NPGDMA, 99.58) was purchased from BLDPharm. All materials were used as received unless otherwise stated.

Instrumentation

Nuclear Magnetic Resonance (NMR) spectroscopy

^1H NMR experiments were recorded using a Bruker Avance II 400 MHz spectrometer with ^{13}C NMR spectra being recorded at 100 MHz. Chemical shifts (δ) are reported in parts per million (ppm) relative to those of an internal standard, tetramethyl silane (TMS) or referenced against a chloroform-d ($CDCl_3$) solvent signal. Samples were analysed in $CDCl_3$ solvent at room temperature and pressure.

Triple-Detection Size Exclusion Chromatography (TD-SEC)

TD-SEC analysis of branched polymers was performed using an Agilent 1260 Infinity II instrument equipped with an autosampler, two Agilent PLgel 10 µm mixed bed columns (and a guard column), coupled to a multi-detector suite, equipped with a dual angle light scattering detector (90:15), refractive index (RI) detector and viscometer, with a 0.5% v/v THF/TEA mobile phase at 40 °C and a flow rate of 1 mL min^{-1}. All samples were prepared at 5 mg mL^{-1} and passed through a 0.2 µm syringe filter before injection (100 µL). From the TD-SEC data yielded, the number-average molecular weight (M_n), weight-average molecular weight (M_W), polymer dispersity (Đ), refractive index increment (dn/dc) and Mark-Houwink values (α) were obtained and analysed using Agilent GPC/SEC software utilising narrow and broad polystyrene standards at 2 mg mL^{-1} for validation (PS narrow: M_W: 87,200 g mol^{-1}, dn/dc: 0.185 mL g^{-1}, [η]: 0.3778 dL g^{-1}).

Molecular Modelling using Spartan software

All molecular modelling and simulations were performed using Spartan software version 24.110 from Wavefunction. Chemical structures were generated in ChemDraw version 22.0.0, copied as SMILES and uploaded into the Spartan Software. Energy minimised calculations were performed to obtain the energy minimised conformations using a gradient-based method, Density Functional Theory (DFT) and a split-valence basis set (6-31G*). The distance between vinyl functionalities was calculated using the 'measure distance' feature under the geometry menu and selecting the appropriate atoms.

Experimental Procedures

All TBRT reactions were performed under a dry, N_2 atmosphere. Example reactions below were conducted at varying solids content and temperatures in either EtOAc or Toluene for 24 hours. AIBN was chosen as a thermal initiator and used at 1.5 mol% per double bond of monomer. Samples (*ca.* 0.1 mL) were taken for ^{1}H NMR spectroscopic analysis in $CDCl_3$ at timepoints t = 0, and t = 24 hours to allow quantification of initial feedstock ratios and conversion of vinyl groups, respectively. A sample of the pure product was taken for ^{1}H NMR spectroscopic analysis in $CDCl_3$ and for TD-SEC analysis in THF.

TBRT of NPGDMA with varying equivalents of DDT conducted at 50 wt% solids in ethyl acetate

In a typical synthesis, NPGDMA (1.2178 g, 5.07 mmol, 0.80 equiv.), DDT (1.2822 g, 6.33 mmol, 1 equiv.), AIBN (0.0250 g, 0.152 mmol) and EtOAc (2.5 g, 2.77 mL, 50 wt%) were added into a 25 mL round-bottomed flask. The solution was stirred and deoxygenated under a nitrogen purge. After 30 minutes, the reaction was sealed, and the solution was stirred and left to telomerise for 24 hours at 70 °C. The reaction was terminated by removal from heat and exposure to air to yield a colourless liquid. The solution was dissolved in THF and precipitated into methanol (1:10 v/v ratio) at room temperature with constant stirring affording a white precipitate. Drying the precipitated sample overnight under high vacuum afforded a colourless material and a sample of the product was taken for ^{1}H NMR spectroscopic analysis and for TD-SEC analysis.

This procedure was performed at targeted $[NPGDMA]_0/[DDT]_0 = 0.70\text{-}1.25$.

TBRT of NPGDMA with varying equivalents of DDT conducted at 30 wt% solids in ethyl acetate

In a typical synthesis, NPGDMA (0.50 g, 2.08 mmol, 0.90 equiv.), DDT (0.4679 g, 2.31 mmol, 1 equiv.), AIBN (0.0103 g, 0.624 mmol) and EtOAc (2.2824 g, 70 wt%) were added into a 25 mL round-bottomed flask. The solution was stirred and deoxygenated under a nitrogen purge. After 30 minutes, the reaction was sealed, and the solution was stirred and left to telomerise for 24 hours at 70 °C. The reaction was terminated by removal from heat and exposure to air to yield a colourless liquid. The solution was dissolved in THF and precipitated into methanol (1:10 v/v ratio) at room temperature with constant stirring affording a white precipitate. Drying the precipitated sample overnight under high vacuum afforded a colourless material and a sample of the product was taken for ^{1}H NMR spectroscopic analysis and for TD-SEC analysis.

This procedure was performed at targeted $[NPGDMA]_0/[DDT]_0 = 0.90\text{-}2.00$.

TBRT of NPGDMA with varying equivalents of DDT conducted at 10 wt% solids in ethyl acetate

In a typical synthesis, NPGDMA (0.50 g, 2.08 mmol, 1.20 equiv.), DDT (0.3509 g, 1.73 mmol, 1 equiv.), AIBN (0.0103 g, 0.624 mmol) and EtOAc (7.7504 g, 90 wt%) were added into a 25 mL round-bottomed flask. The solution was stirred and deoxygenated under a nitrogen purge. After 30 minutes, the reaction was sealed, and the solution was stirred and left to telomerise for 24 hours at 70 °C. The reaction was terminated by removal from heat and exposure to air to yield a colourless liquid. The solution was dissolved in THF and precipitated into methanol (1:10 v/v ratio) at room temperature with constant stirring affording a white precipitate. Drying the precipitated sample overnight under high vacuum afforded a colourless material and a sample of the product was taken for ^{1}H NMR spectroscopic analysis and for TD-SEC analysis.

This procedure was performed at targeted $[NPGDMA]_0/[DDT]_0 = 1.20 - 5.00$.

TBRT of NPGDMA with varying equivalents of DDT conducted at 50 wt% solids at 90 °C in toluene

In a typical synthesis, NPGDMA (0.50 g, 2.08 mmol, 0.80 equiv.), DDT (0.5264 g, 2.60 mmol, 1 equiv.), AIBN (0.0103 g, 0.624 mmol) and toluene (1.0367 g, 50 wt%) were added into a 25 mL round-bottomed flask. The solution was stirred and deoxygenated under a nitrogen purge. After 30 minutes, the reaction was sealed, and the solution was stirred and left to telomerise for 24 hours at 90 °C. The reaction was terminated by removal from heat and exposure to air to yield a colourless liquid. The solution was dissolved in THF and precipitated into methanol (1:10 v/v ratio) at room temperature with constant stirring affording a white precipitate. Drying the precipitated sample overnight under high vacuum afforded a colourless gel and a sample of the product was taken for ^{1}H NMR spectroscopic analysis and for TD-SEC analysis.

This procedure was performed at targeted $[NPGDMA]_0/[DDT]_0 = 0.80\text{-}1.30$.

TBRT of NPGDMA with varying equivalents of DDT conducted at 50 wt% solids at 100 °C in toluene

In a typical synthesis, NPGDMA (0.50 g, 2.08 mmol, 0.80 equiv.), DDT (0.5264 g, 2.60 mmol, 1 equiv.), AIBN (0.0103 g, 0.624 mmol) and toluene (1.0367 g, 50 wt%) were added into a 25 mL round-bottomed flask. The solution was stirred and deoxygenated under a nitrogen purge. After 30 minutes, the reaction was sealed, and the solution was stirred and left to telomerise for 24 hours at 100 °C. The reaction was terminated by removal from heat and exposure to air to yield a colourless liquid. The solution was dissolved in THF and precipitated into methanol (1:10 v/v ratio) at room temperature with constant stirring affording a white precipitate. Drying the precipitated sample overnight under high vacuum afforded a colourless material and a sample of the product was taken for ^{1}H NMR spectroscopic analysis and for TD-SEC analysis.

This procedure was performed at targeted $[NPGDMA]_0/[DDT]_0 = 0.80\text{-}1.30$.
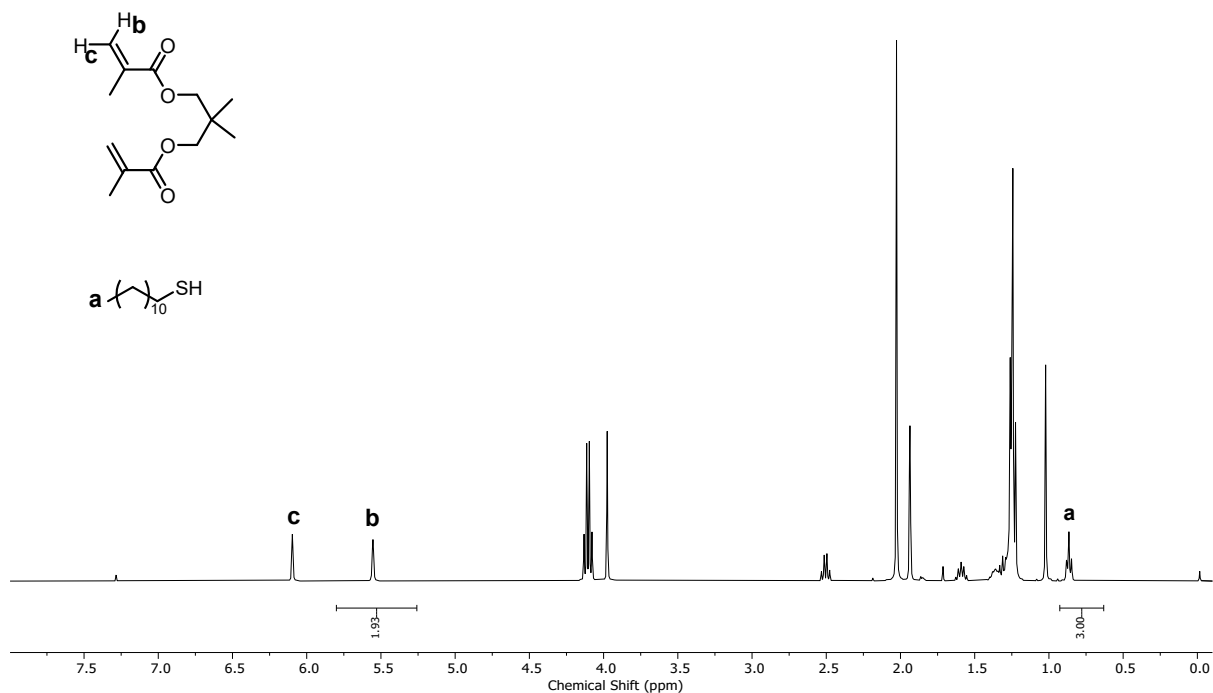
Supplementary figures and tables

Figure S1. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of the TBRT of NPGDMA at t = 0 hours used to calculate [NPGDMA]$_0$/[DDT]$_0$. In this case (50 wt% solids) a ratio of 0.96 was determined (See manuscript Table 1).

$$\frac{[NPGDMA]_0}{[DDT]_0} = \left(\frac{\left(\int^{H_b}\frac{}{2}\right)}{\left(\int^{H_a}\frac{}{3}\right)}\right)$$

Equation S1. Calculation of the ratio of NPGDMA to DDT within reaction mixtures at t = 0 hours. Calculations are based on comparison of the integrals from chemical shifts of NPGDMA (H vinyl – 5.55 ppm) and DDT (0.85 ppm), following normalisation of the methyl group on DDT at 0.85 ppm to 3H.
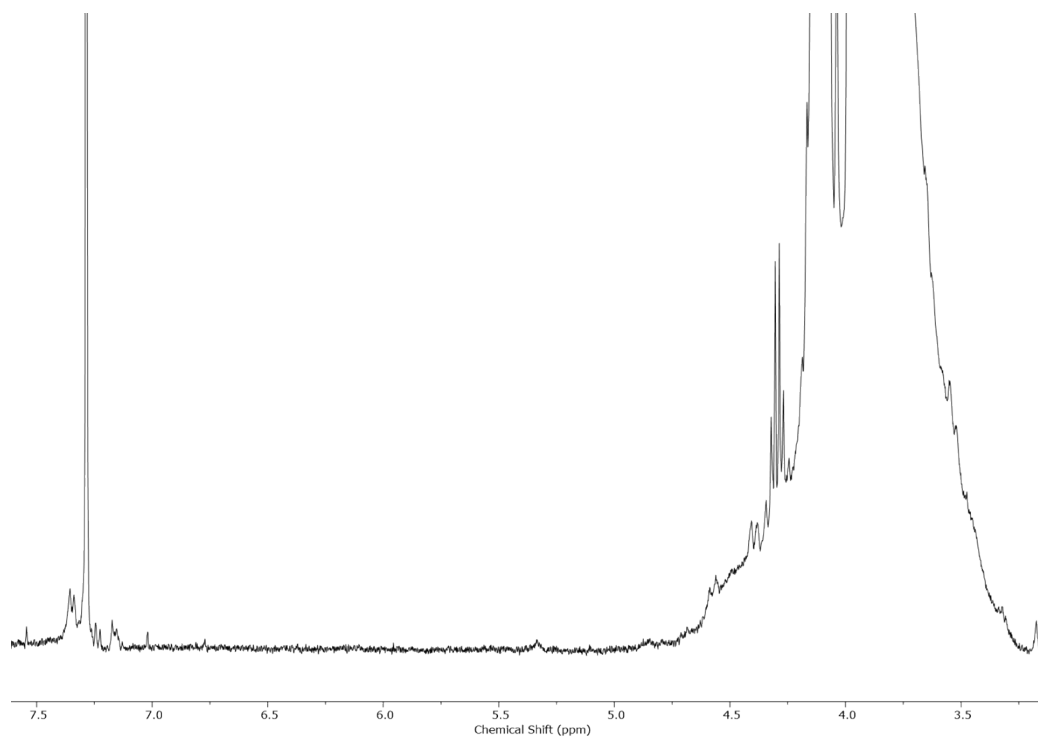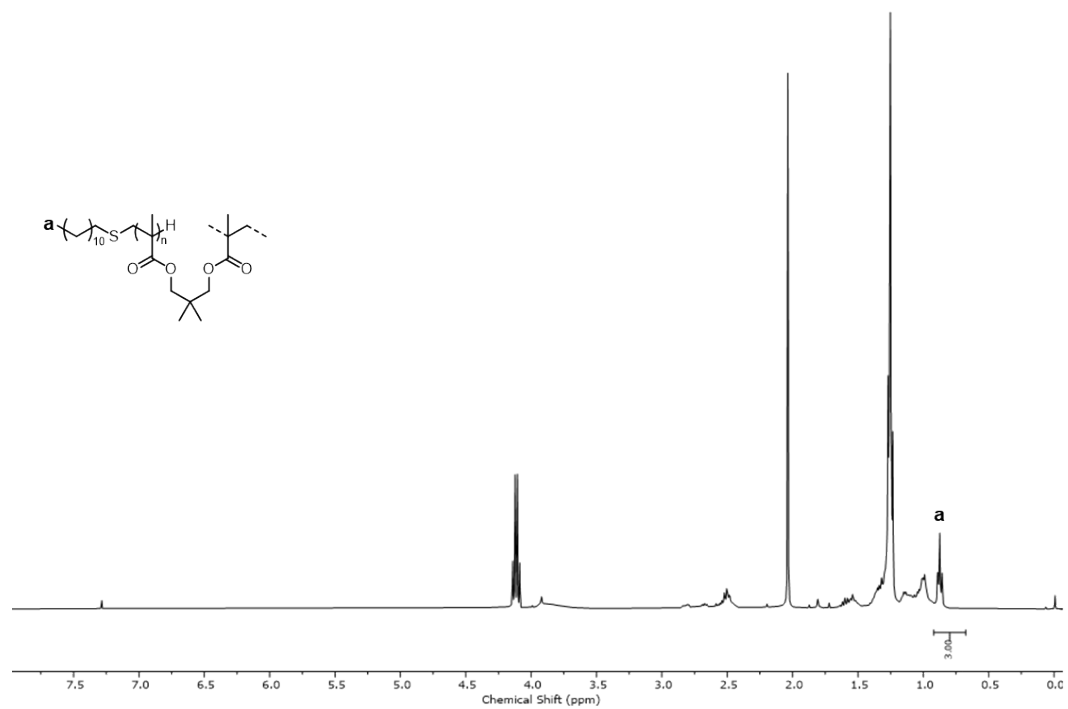
Figure S2. ^1H NMR (400 MHz, CDCl$_3$) spectra (including zoom in) of the TBRT of NPGDMA crude reaction mixture at t = 24 hours used to calculate [NPGDMA]$_F$/[DDT]$_F$. ([NPGDMA]$_0$/[DDT]$_0$ = 0.96) (note absence of vinyl resonances).

$$Vinyl\ Consumption\ (\%) = \left(\frac{intergral\ at\ t = 0 - integral\ at\ t = f}{intergral\ at\ t = 0}\right) \times 100$$

Equation S2. Calculation of the monomer consumption of NPGDMA vinyl groups at T=t, by ^{1}H NMR analysis (400 MHz, CDCl$_3$). Calculations were made using the integrals from the chemical shift at 5.5 ppm and 6.08 ppm at t = 0 and t = 24 hours following normalisation of the methyl group on DDT at 0.85 ppm to 3H.
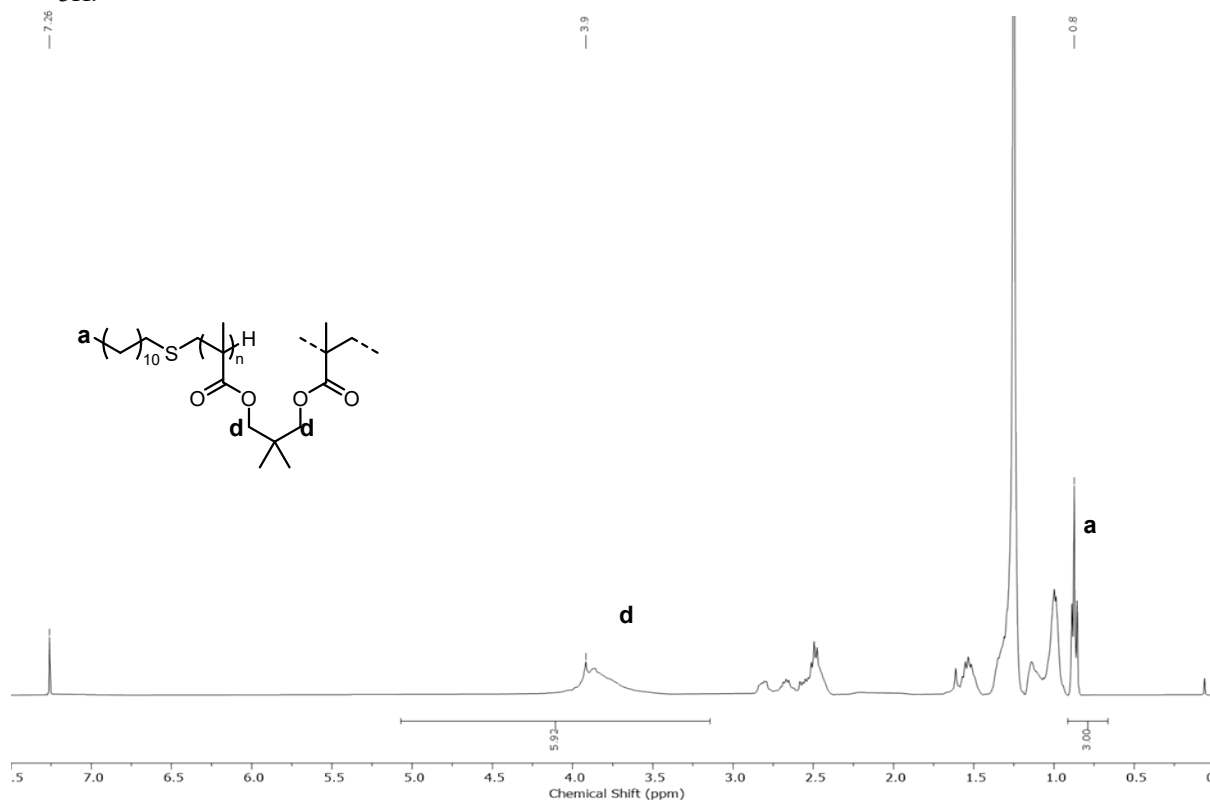
Figure S3. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of the purified p(DDT-NPGDMA) sample showing the [NPGDMA]$_{final}$/[DDT]$_{final}$ = 1.48 ([NPGDMA]$_0$/[DDT]$_0$ = 0.96).

$$\frac{[NPGDMA]_f}{[DDT]_f} = \left(\frac{\left(\int \frac{H_d}{4}\right)}{\left(\int \frac{H_a}{3}\right)}\right)$$

Equation S3. Calculation of the ratio of NPGDMA to DDT within the purified product. Calculations are based on comparison of the integrals from chemical shifts of NPGDMA (-CH$_2$CH$_2$-, 4.26 ppm) and DDT (-CH$_3$, 0.88 ppm), following normalisation of the methyl group on DDT at 0.87 ppm to 3H.

$$\frac{[c]}{[MVT]_F} = 1 - \left(\frac{1}{[MVT]_F/[Tel]_F}\right)$$

Equation S4. General calculation of the ratio of cycles to MVT residues in a purified TBRT polymer.
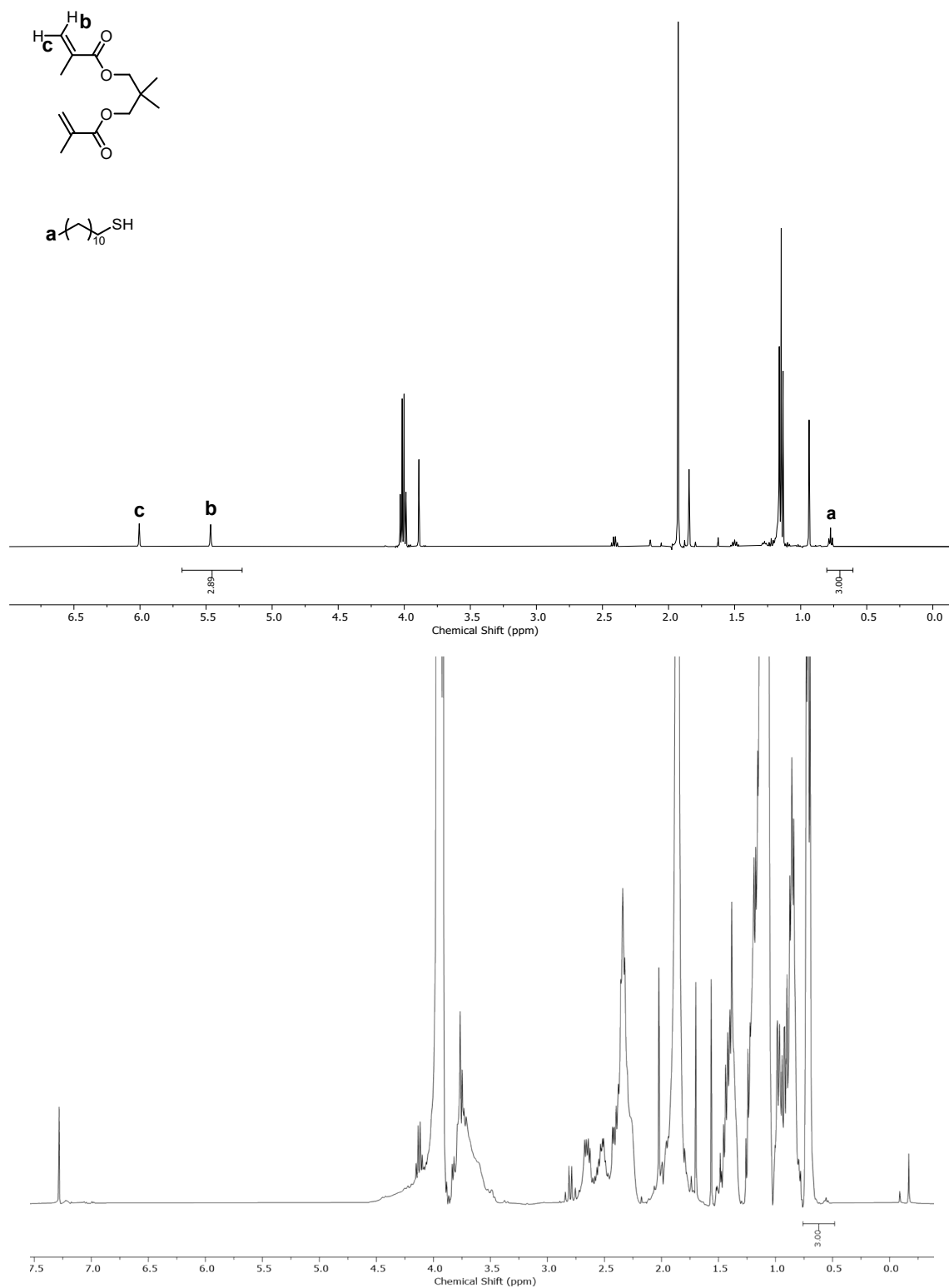
Figure S4. ^{1}H NMR (400 MHz, CDCl$_3$) spectra of p(DDT-NPGDMA) synthesis at t = 0 hours (top) and t = 24 hours conducted at 30 wt% solids and 70 °C ([NPGDMA]$_0$/[DDT]$_0$ = 1.45).
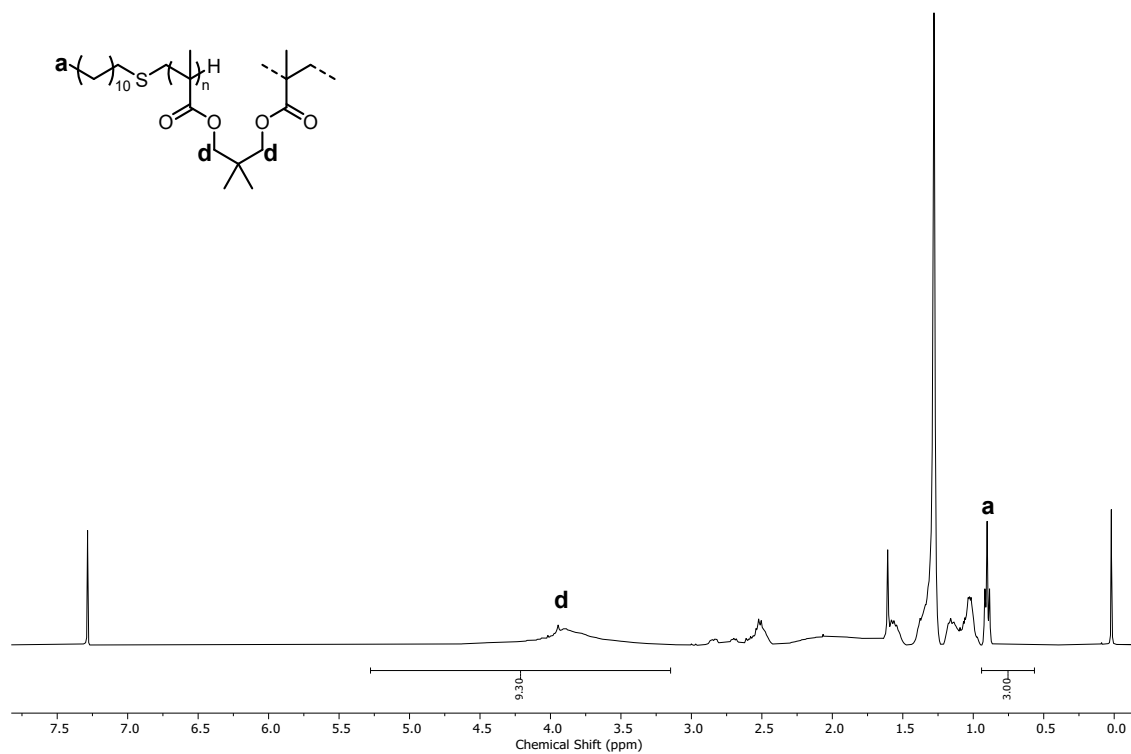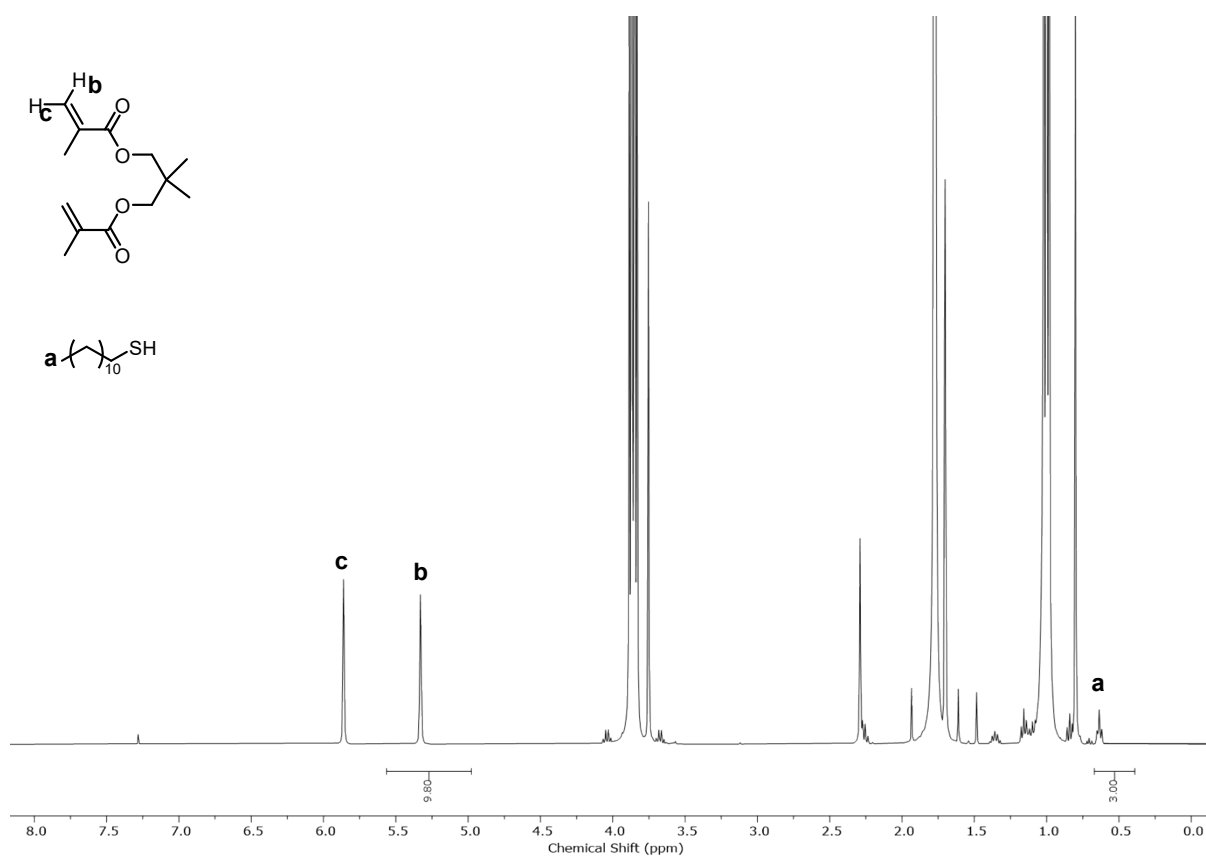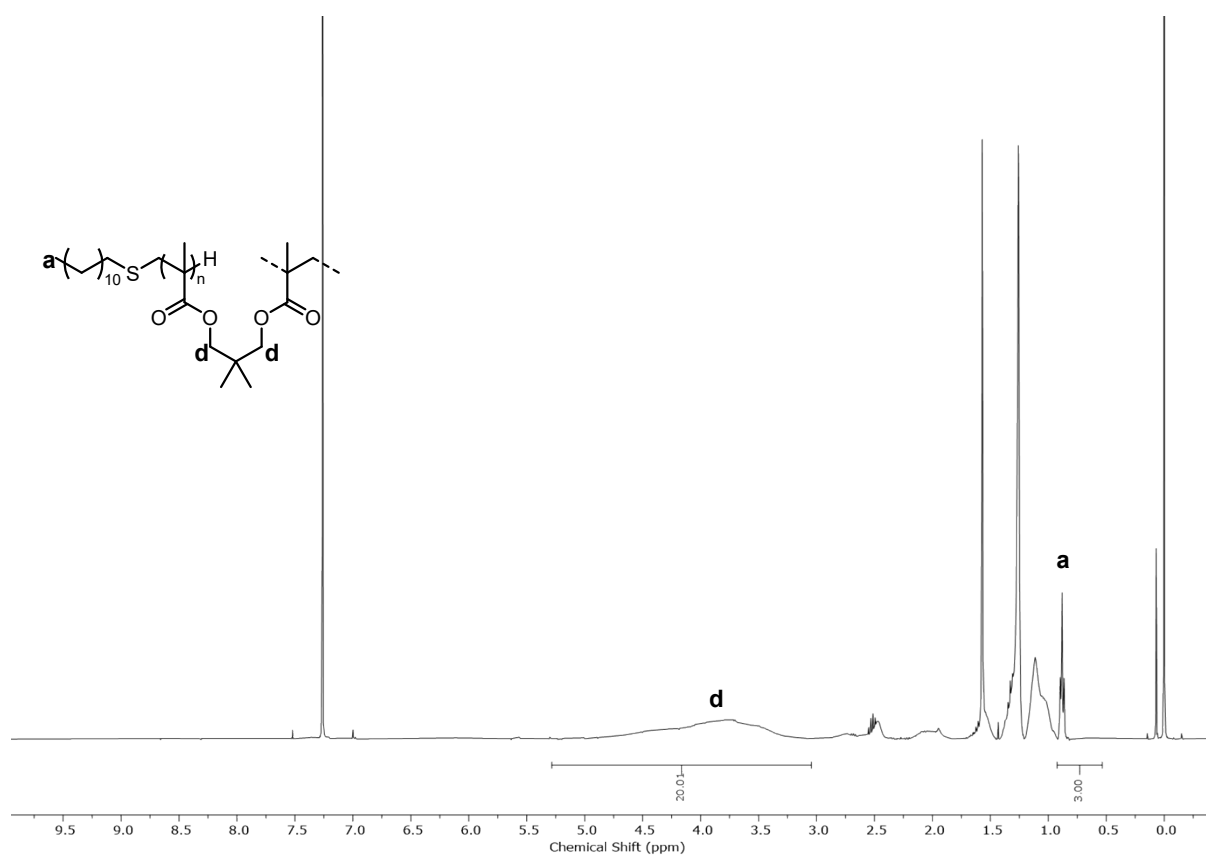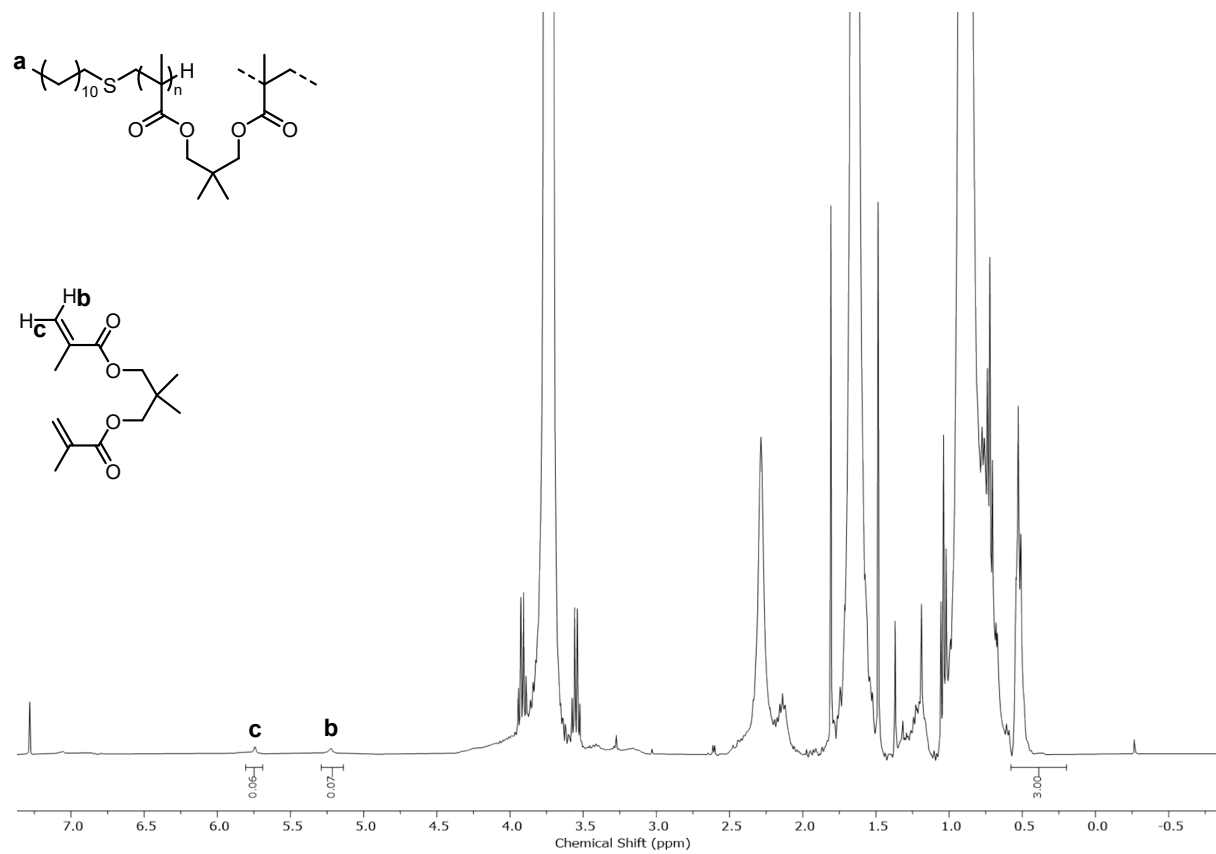
Figure S5. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of the purified sample of p(DDT-NPGDMA) synthesised at 30 wt% solids and 70 °C ([NPGDMA]$_0$/[DDT]$_0$ = 1.45) - [NPGDMA]$_F$/[DDT]$_F$ = 2.33.

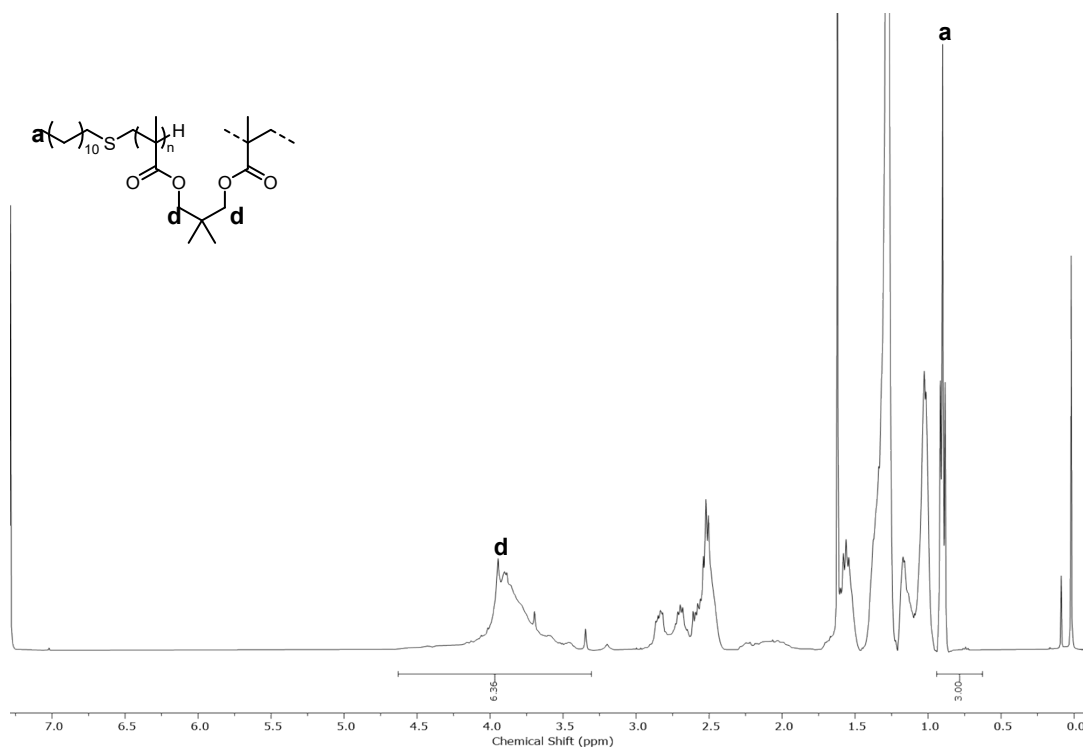**Figure S7.** ^{1}H NMR (400 MHz, CDCl₃) spectra of the purified sample of p(DDT-NPGDMA) synthesised at 10 wt% solids and 70 °C ([NPGDMA]$_0$/[DDT]$_0$ = 4.90) – crude reaction mixture after t=24 hours (top) and purified sample (bottom) showing [NPGDMA]$_F$/[DDT]$_F$ = 5.00.
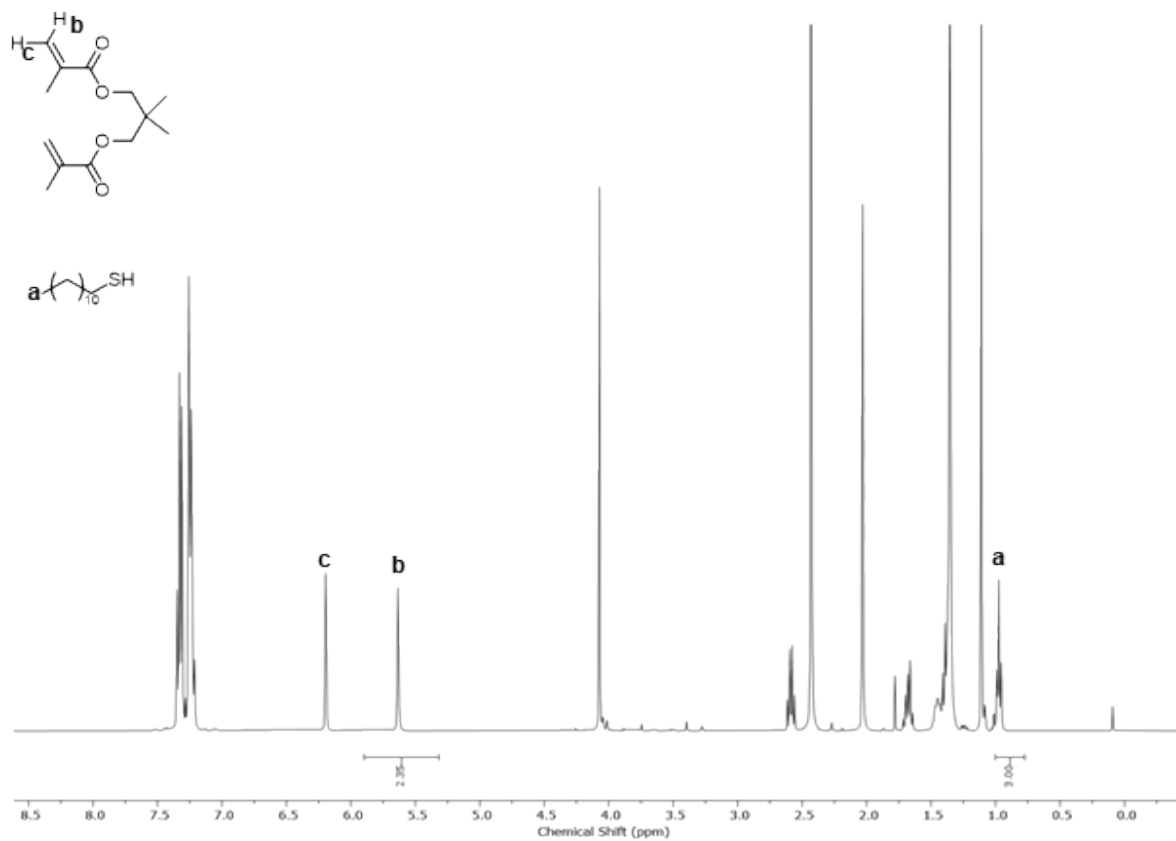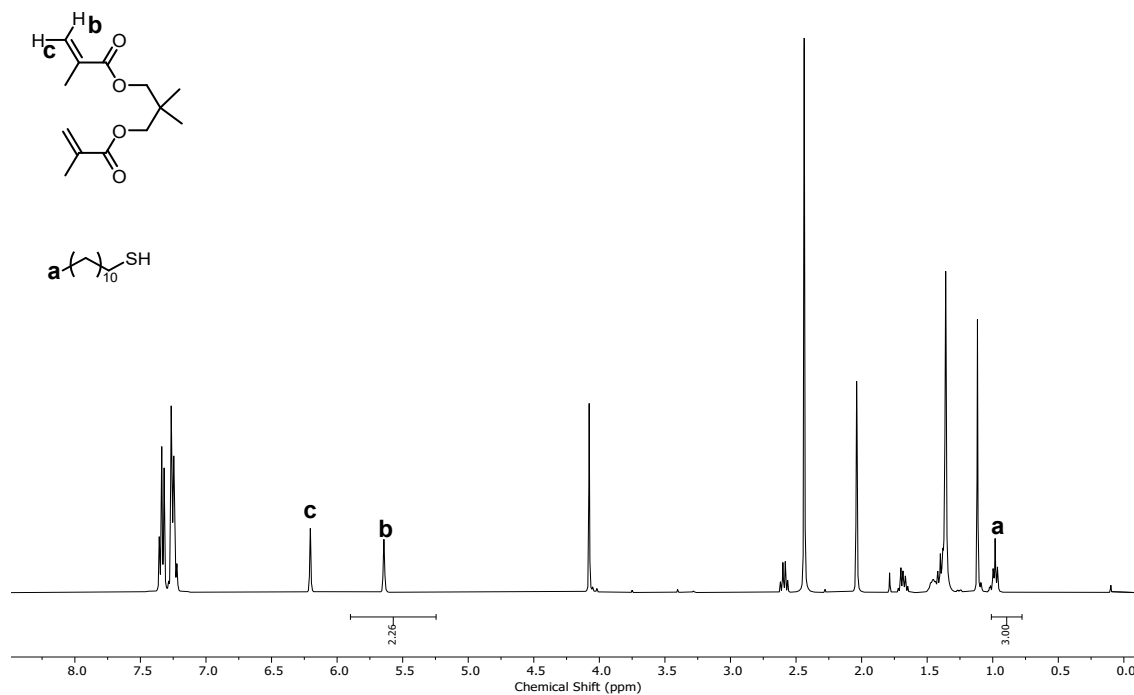
Figure S8. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of p(DDT-NPGDMA) synthesis conducted at 50 wt% solids and 90 °C (t = 0 hours) showing the [NPGDMA]$_0$/[DDT]$_0$ = 1.18.
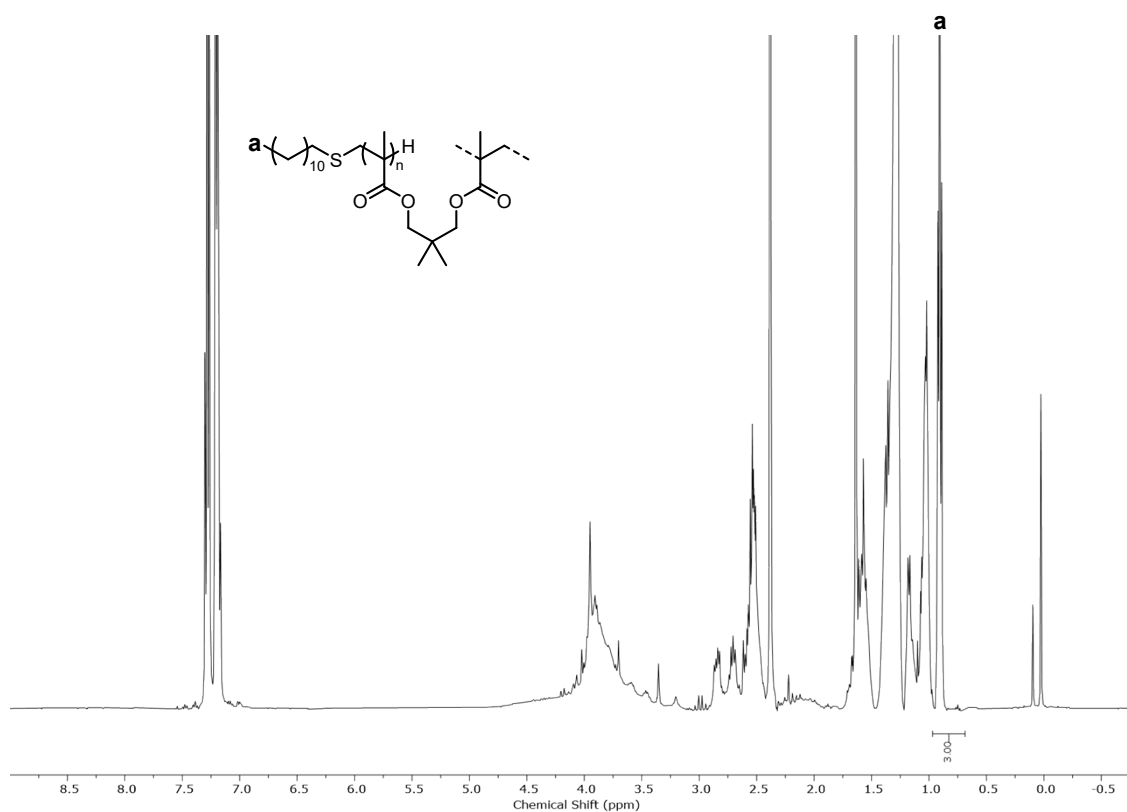
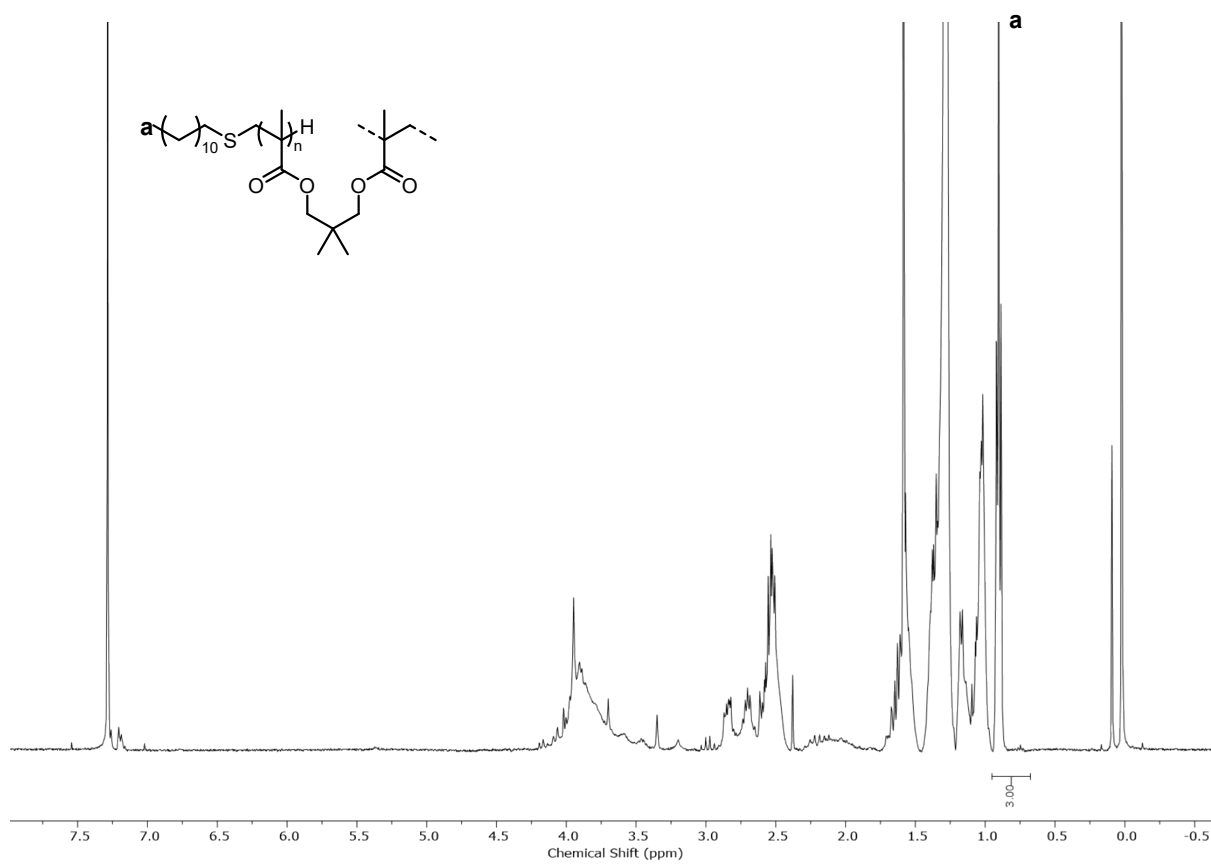**Figure S9.** ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of p(DDT-NPGDMA) synthesis conducted at 50 wt% solids and 90 °C (crude reaction mixture t = 24 hours).

Figure S10. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of the purified sample of p(DDT-NPGDMA) synthesised at 50 wt% solids and 90 °C showing the [NPGDMA]$_F$/[DDT]$_F$ = 1.59.

Figure S11. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of *p*(DDT-NPGDMA) synthesis conducted at 50 wt% solids and 100 °C at t = 0 hours showing the [NPGDMA]$_0$/[DDT]$_0$ = 1.13.

Figure S12. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of *p*(DDT-NPGDMA) synthesis conducted at 50 wt% solids and 100°C at t = 24 hours (crude reaction mixture).
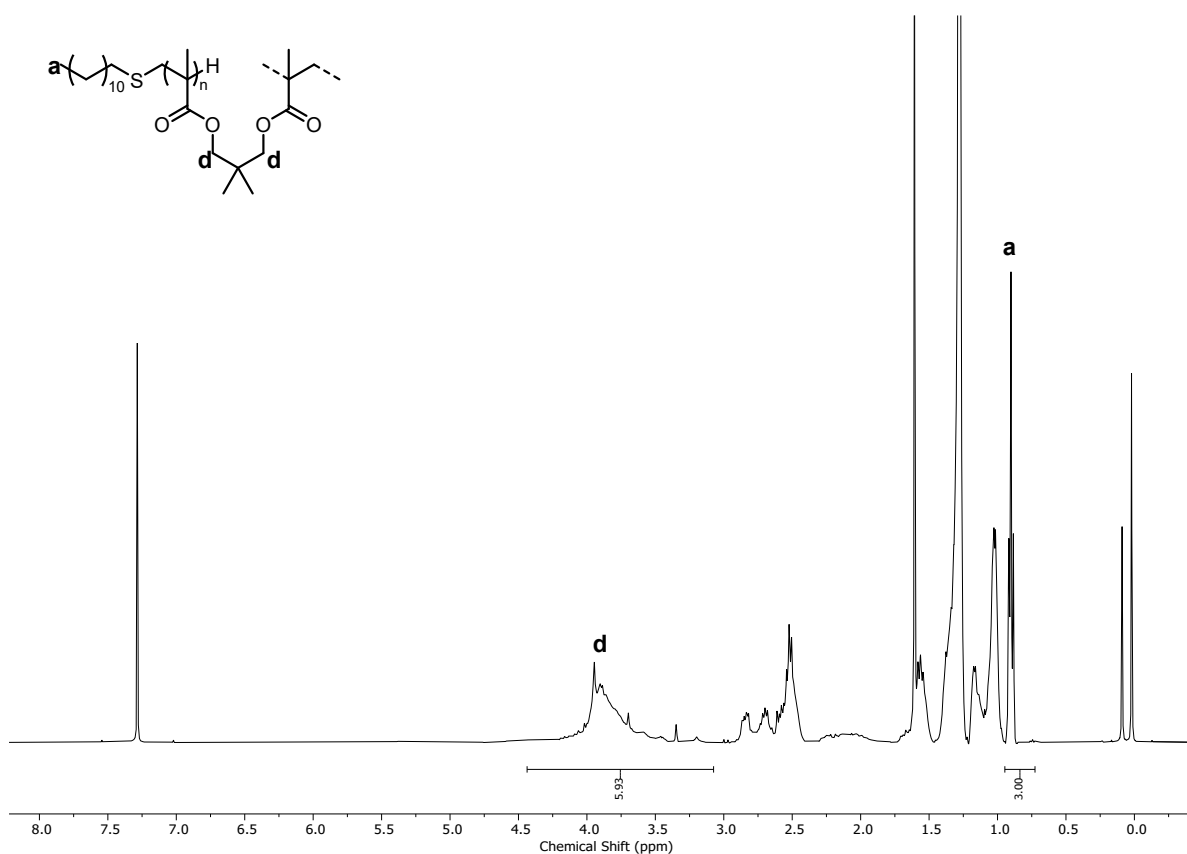
Figure S13. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of the purified sample of p(DDT-NPGDMA) synthesised at 50 wt% solids and 100 °C showing the [NPGDMA]$_F$/[DDT]$_F$ = 1.48.
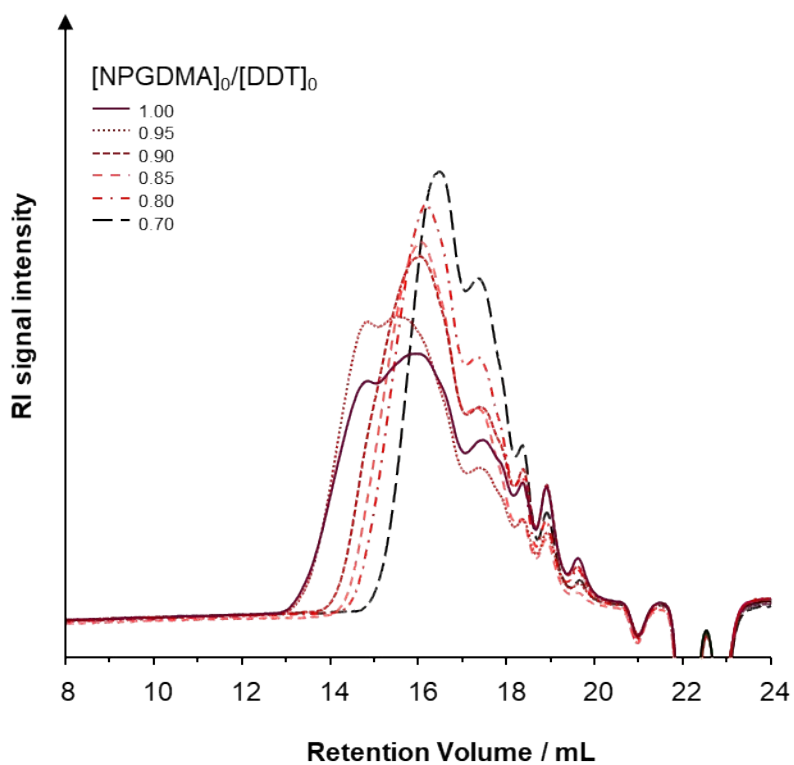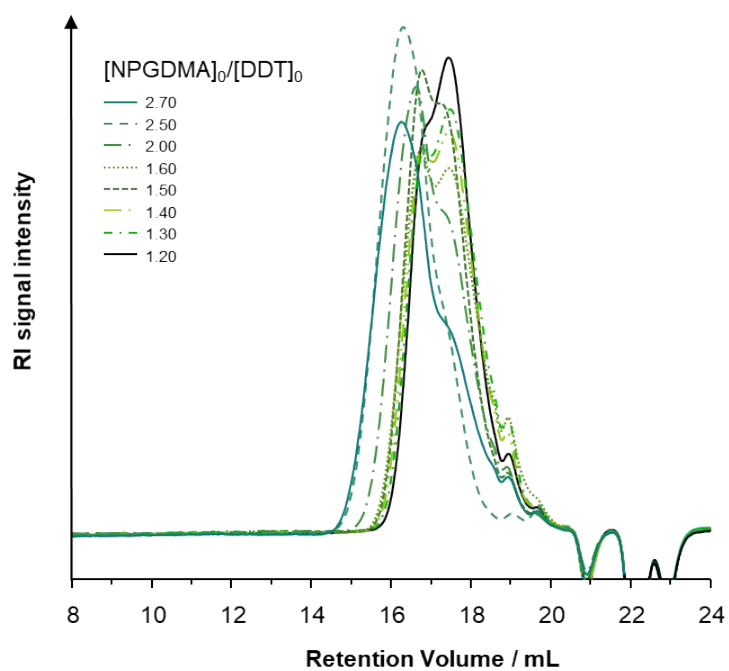

Figure S14. TD-SEC (THF eluent: refractive index (RI) detector signal) showing the molecular weight distributions of branched polymers derived from various [NPGDMA]$_0$/[DDT]$_0$ conducted at 50 wt% solids (70 °C; EtOAc).

Figure S15 TD-SEC (THF eluent: refractive index (RI) detector signal) showing the molecular weight distributions of branched polymers derived from various $[NPGDMA]_0/[DDT]_0$ ratios conducted at 10 wt% solids (70 °C; EtOAc).
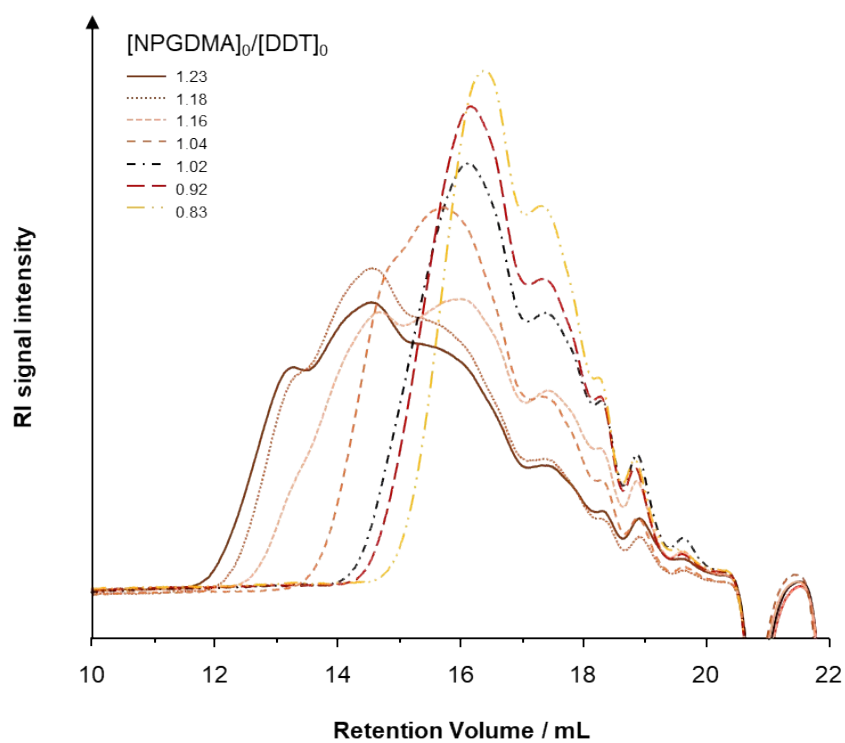

Figure S16 TD-SEC (THF eluent: refractive index (RI) detector signal) showing the molecular weight distributions of branched polymers derived from various $[NPGDMA]_0/[DDT]_0$ ratios conducted at 90 °C (50 wt% solids; toluene).
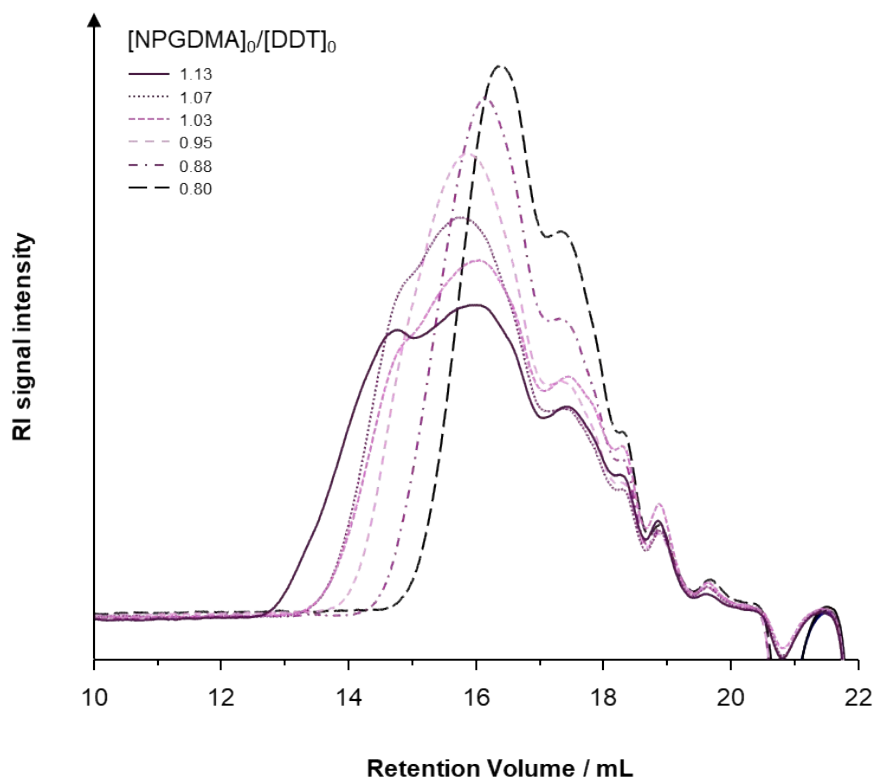
Figure S17 TD-SEC (THF eluent: refractive index (RI) detector signal) showing the molecular weight distributions of branched polymers derived from various $[\text{NPGDMA}]_0/[\text{DDT}]_0$ ratios conducted at 100 °C (50 wt% solids).