

Utilising the effect of reaction concentration to tune the physical properties of hyperbranched polymers synthesised using Transfer-dominated Branching Radical Telomerisation (TBRT)

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Experimental

Materials

2,2'-Azobis(2-methylpropionitrile) (AIBN, 98 %), bis(2-methacryloyl)oxyethyl disulphide (DSDMA), CDCl₃ (99.8 atom% D) and ethylene glycol dimethacrylate (EGDMA, 98 %) were purchased from Sigma Aldrich. Ethyl acetate (EtOAc, analytical grade), methanol (MeOH, analytical grade 99.9 %) and tetrahydrofuran (THF, HPLC-grade) were purchased from Fisher. 1-Dodecanethiol (DDT, 98 %) was purchased from Alfa Aesar. All materials were used as received unless otherwise stated.

Methods

¹H and ¹³C experiments were recorded on a Bruker AMX-400 MHz spectrometer. Samples were analysed in deuterated chloroform (CDCl₃) at room temperature unless otherwise stated. Chemical shifts (δ) are reported in parts per million (ppm) relative to the known solvent residual peak ($\delta = 7.26$ ppm, 77.16 ppm). All TD-SEC analyses of branched polymers were performed using a Malvern Viscotek instrument using GPCmax VE2001 autosampler, two Viscotek T6000M columns (and a guard column), a refractive index (RI) detector VE3580 and a 270 Dual Detector (light scattering and viscometer) with a mobile phase of THF containing 2 v/v % of Triethylamine at 35 °C and a flow-rate of 1 mL/min. All samples were dissolved at 10 mg/mL with THF as eluent and passed through a 200 nm PTFE syringe filter prior to injection (100 μ L). From TD-SEC results, the number average (M_n) and weight average (M_w) molecular weights, Dispersity (\mathcal{D}), molecular weight distribution and intrinsic viscosity of the polymers were estimated with narrow and broad polystyrene standards (Viscotek, $M_w = 105,000$ g mol⁻¹, $\mathcal{D} = 1.022$ and $M_w = 245,000$ g mol⁻¹, $\mathcal{D} = 2.272$ respectively) for calibration.

Example TBRT of EGDMA with varying equivalents of DDT conducted at 0 wt% EtOAc

In a typical synthesis, EGDMA (3.00 g, 15.1 mmol, 1 equiv.), DDT (6.81 g, 33.6 mmol, 2.22 equiv.) and AIBN (74.4 mg, 0.453 mmol) were added into a round bottom flask (25 mL) equipped with a magnetic stirrer bar. The resulting solution was purged with N₂ for 15 minutes. At this point a sample was withdrawn (*ca.* 100 μ L) and diluted in CDCl₃ allowing for

quantification of $[EGDMA]_0/[DDT]_0$ by ^1H NMR. The reaction was sealed and left to stir at 70 °C for 24 hours and was subsequently terminated by exposure to air and cooled. At this point, a sample (*ca.* 200 μL) was taken for quantification of vinyl conversion by ^1H NMR. Integrals of the vinyl protons (5.57 ppm and 6.12 ppm) were compared with integration of the vinyl protons corresponding to the t_0 NMR to determine conversion. The reaction was diluted with THF and precipitated into methanol (1:10 ratio) at room temperature to remove excess DDT, affording a white precipitate. The polymer was then dried *in vacuo* at 40 °C for 48 hours and characterised *via* ^1H NMR in CDCl_3 and TD-SEC using THF/TEA eluent (98/2 v/v %) using a narrow and broad *p*(styrene) standard calibration.

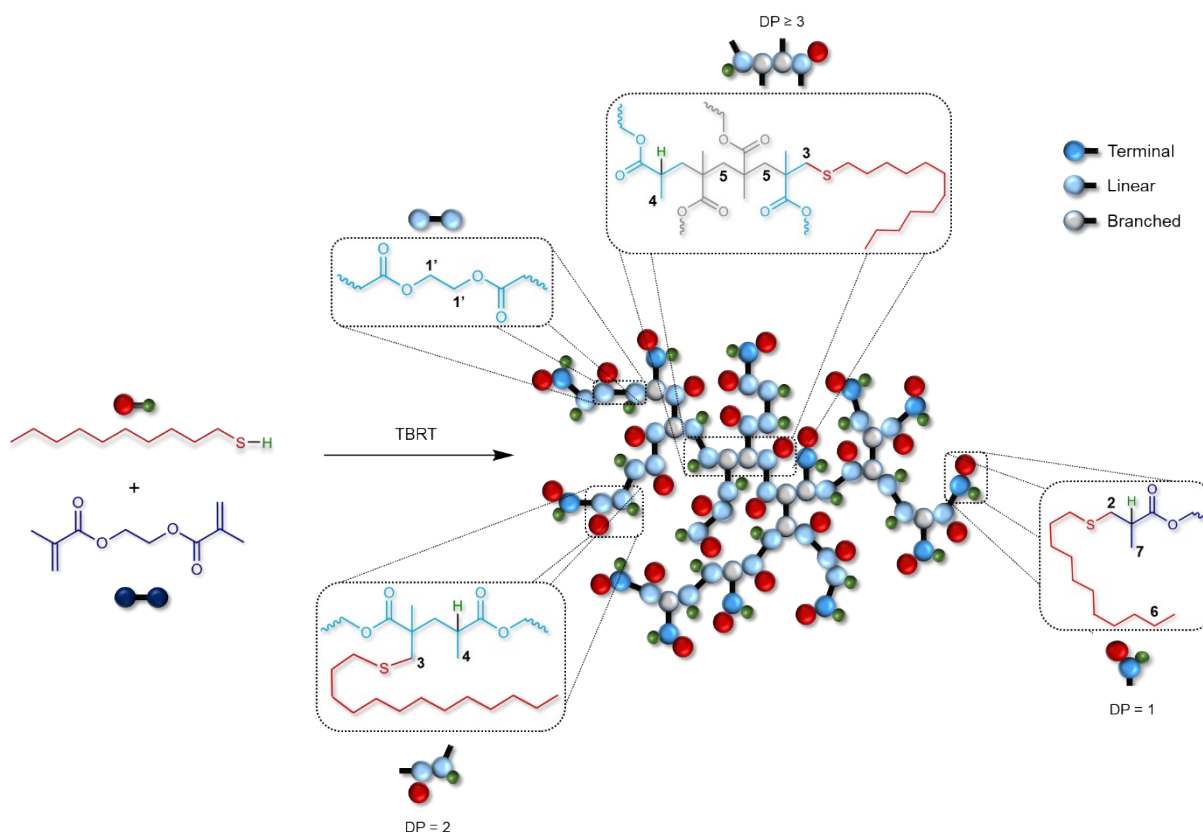
Example TBRT of EGDMA with varying equivalents of DDT conducted at 90 wt% EtOAc

In a typical synthesis conducted at high solvent dilution, EGDMA (3.00 g, 15.1 mmol, 1 equiv.), DDT (1.45 g, 7.21 mmol, 0.476 equiv.) and AIBN (74.4 mg, 0.453 mmol) were added into a round bottom flask (100 mL) equipped with a magnetic stirrer bar. EtOAc was added (44.4 mL, 90 wt%) and the resulting solution was purged with N_2 for 15 minutes. At this point a sample was withdrawn (*ca.* 200 μL) and diluted in CDCl_3 allowing for quantification of $[EGDMA]_0/[DDT]_0$ by ^1H NMR. The reaction was sealed and left to stir at 70 °C for 24 hours. The reaction was sealed and left to stir at 70 °C for 24 hours and was subsequently terminated by exposure to air and cooled. At this point, a sample (*ca.* 200 μL) was taken for quantification of vinyl conversion by ^1H NMR. Integrals of the vinyl protons (5.57 ppm and 6.12 ppm) were compared with integration of the vinyl protons corresponding to the t_0 NMR to determine conversion. The reaction was concentrated and precipitated into methanol (1:10 ratio) at room temperature, affording a white solid precipitate. The polymer was then dried *in vacuo* at 40 °C for 48 hours and characterised *via* ^1H NMR in CDCl_3 and TD-SEC using THF/TEA eluent (98/2 v/v %) using a narrow and broad *p*(styrene) standard calibration.

General procedure for TBRT of DSDMA with DDT conducted at 50 wt% EtOAc

DSDMA (1.00 g, 3.44 mmol, 1 equiv.), DDT (0.928 g, 4.59 mmol, 1.33 equiv.) and AIBN (17.0 mg, 0.103 mmol) were added into a round bottom flask (10 mL) equipped with a magnetic stirrer bar. The reaction solvent, EtOAc (21.4 mL, 50 wt%), was then added and the resulting solution was purged with N_2 for 15 minutes. A sample was withdrawn (*ca.* 100 μL) and diluted in CDCl_3 allowing for quantification of $[DSDMA]_0/[DDT]_0$ by ^1H NMR. The reaction was sealed and left to stir at 70 °C for 24 hours and was subsequently terminated by exposure

to air and cooled. At this point, a sample (*ca.* 200 μL) was taken for quantification of vinyl conversion by ^1H NMR. The solution was concentrated and precipitated into cold methanol (1:10 ratio), affording a white precipitate. The polymer was then dried *in vacuo* at 40 $^\circ\text{C}$ for 48 hours and characterised *via* ^1H NMR in CDCl_3 and TD-SEC using THF/TEA eluent (98/2 v/v %) using a narrow and broad *p*(styrene) standard calibration.



Scheme S1 Schematic representation of the structural components within the branched polyester product, highlighting terminal (DP = 1), linear (DP = 2) and branched units (DP \geq 3).

$$(I_{C_1'} - I_{C_2}) - (I_{C_3} \cdot 2)$$

Equation S1 Calculation of the mol fraction of branched structural sub-units within the purified HBPs. Calculations are based on the subtraction of the integrals from the terminal carbons (C2; 34.50 ppm) from the total EGDMA (C1; 62.34 ppm) and linear carbons (C3; 35.51 ppm).

Table S1 Detailed analysis of a series of polymers generated *via* TBRT, at the highest ratio of [EGDMA]₀/[DDT]₀ achieved at each EtOAc wt% before gelation at 70 °C (Initiator: 1.5 mole% AIBN based on vinyl bonds). ^a Determined by ¹H NMR of t₀ sample in CDCl₃. ^b Determined by ¹H NMR of purified and dried material in CDCl₃. ^c Determined by Equation 1 employing inverse-gated ¹³C NMR of the purified and dried material in CDCl₃.

EtOAc (wt%)	NMR (CDCl ₃)			DSC		
	[EGDMA] ₀ /[DDT] ₀ ^a	[EGDMA] _F /[DDT] _F ^b	Branched units (%) ^c	Linear units (%) ^c	Terminal units (%) ^c	T _g (°C) ^d
0	0.45	0.98	41	39	20	-48
10	0.525	1.05	39	40	21	-47
20	0.60	0.95	39	43	19	-45
30	0.65	0.85	33	45	22	-46
40	0.75	1.00	35	45	20	-46
50	0.85	1.02	41	34	25	-47
60	1.00	1.06	-	-	-	-47
70	1.18	1.18	-	-	-	17
80	1.43	1.25	-	-	-	28
90	2.10	1.83	-	-	-	41

^d Calculated by DSC thermograms performed at a heating and cooling rate of 10 °C min⁻¹. The T_g values were calculated based on the second heat cycle.

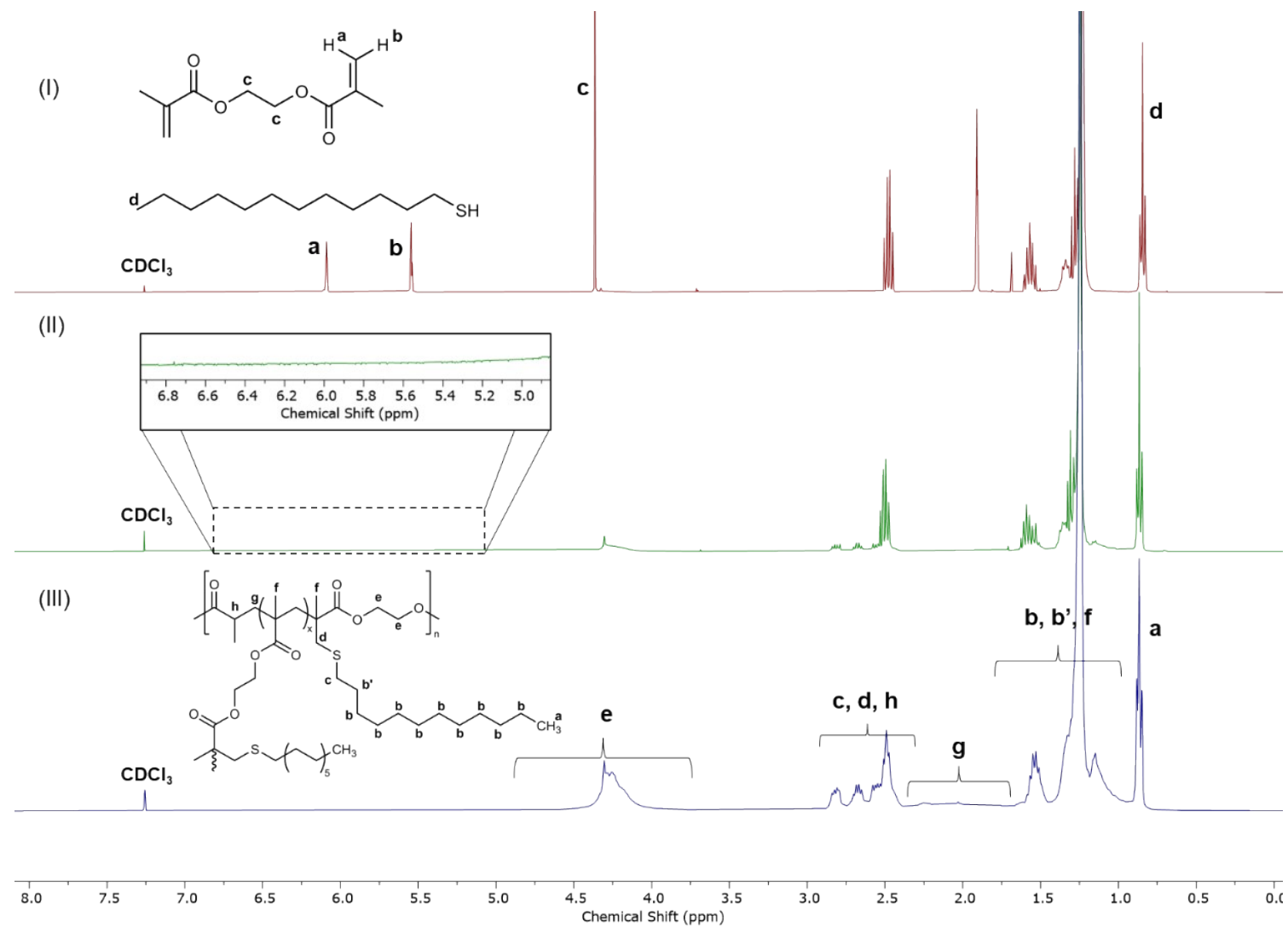


Figure S1 ^1H NMR spectra (400 MHz, CDCl_3) of [EGDMA]/[DDT] conducted at 0 wt% EtOAc. (I) $[\text{EGDMA}]_0/[\text{DDT}]_0 = 0.450$, (II) the crude sample after 24 hours, and (III) the purified and dried material, $[\text{EGDMA}]_x/[\text{DDT}]_x = 0.98$.

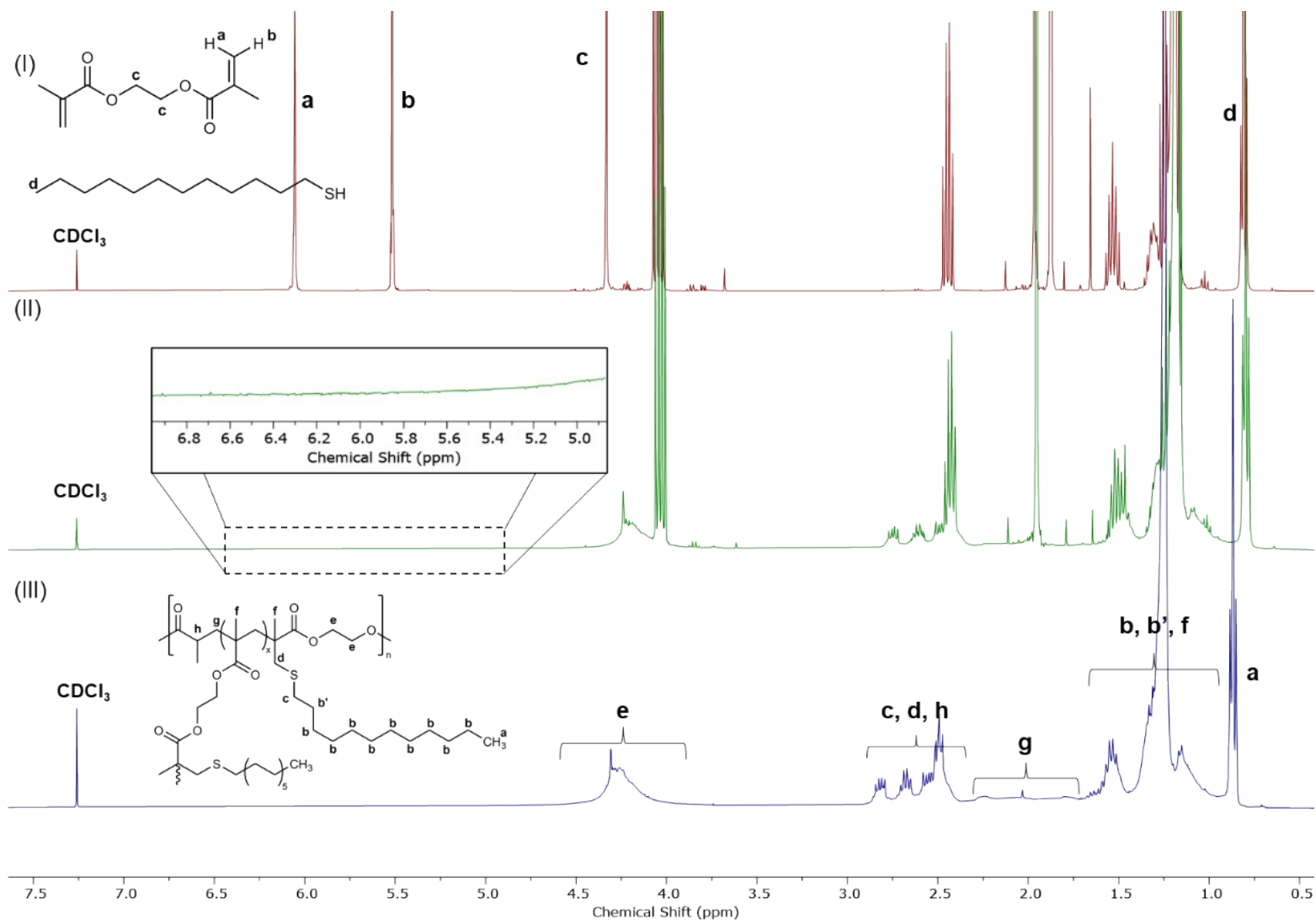


Figure S2 ^1H NMR spectra (400 MHz, CDCl_3) of [EGDMA]/[DDT] conducted at 10 wt% EtOAc. (I) $[\text{EGDMA}]_0/[\text{DDT}]_0 = 0.525$, (II) the crude sample after 24 hours, and (III) the purified and dried material, $[\text{EGDMA}]_x/[\text{DDT}]_x = 1.05$.

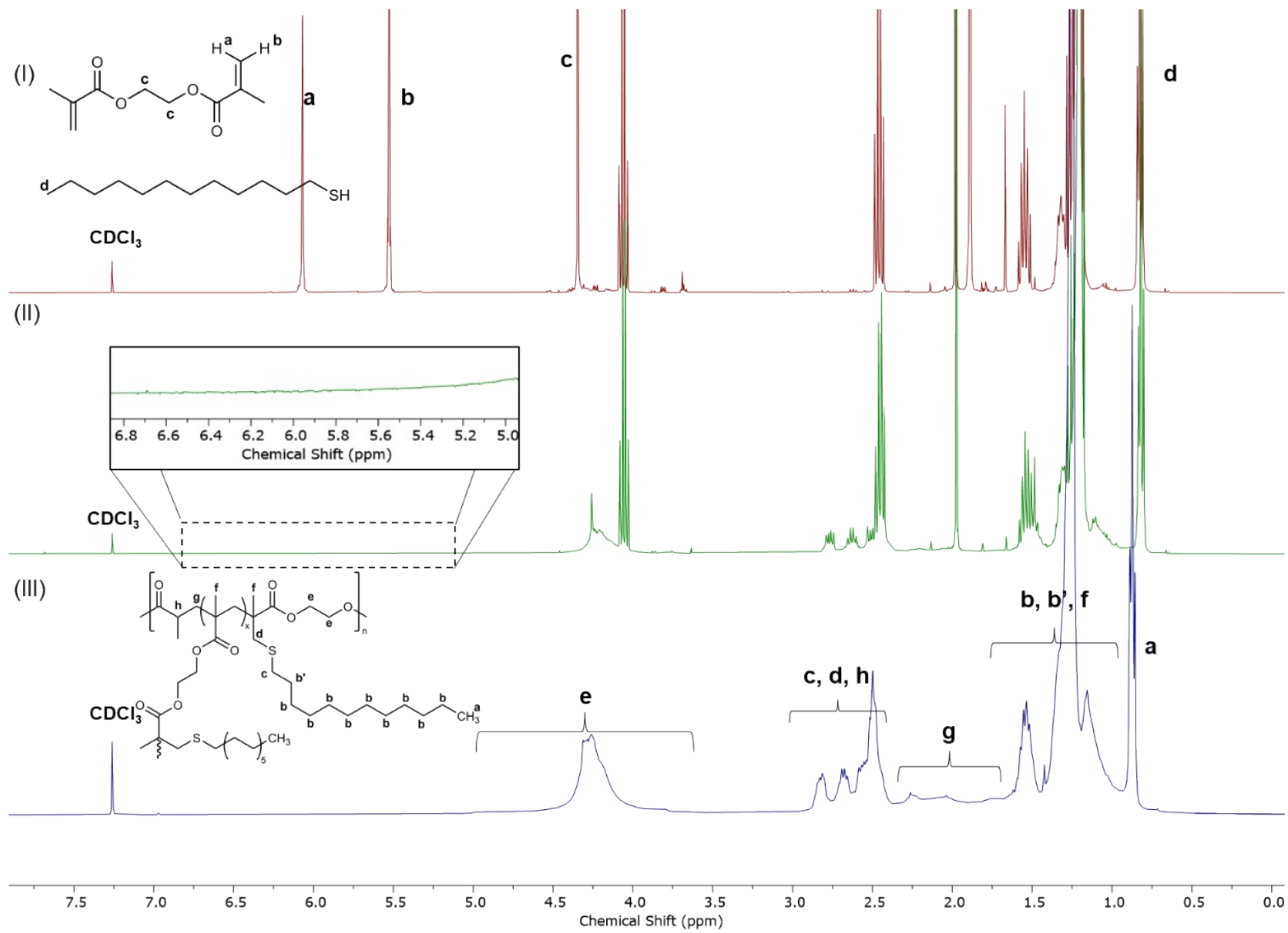


Figure S3 ^1H NMR spectra (400 MHz, CDCl_3) of $[\text{EGDMA}]/[\text{DDT}]$ conducted at 20 wt% EtOAc. (I) $[\text{EGDMA}]_0/[\text{DDT}]_0 = 0.600$, (II) the crude sample after 24 hours, and (III) the purified and dried material, $[\text{EGDMA}]_F/[\text{DDT}]_F = 0.95$.

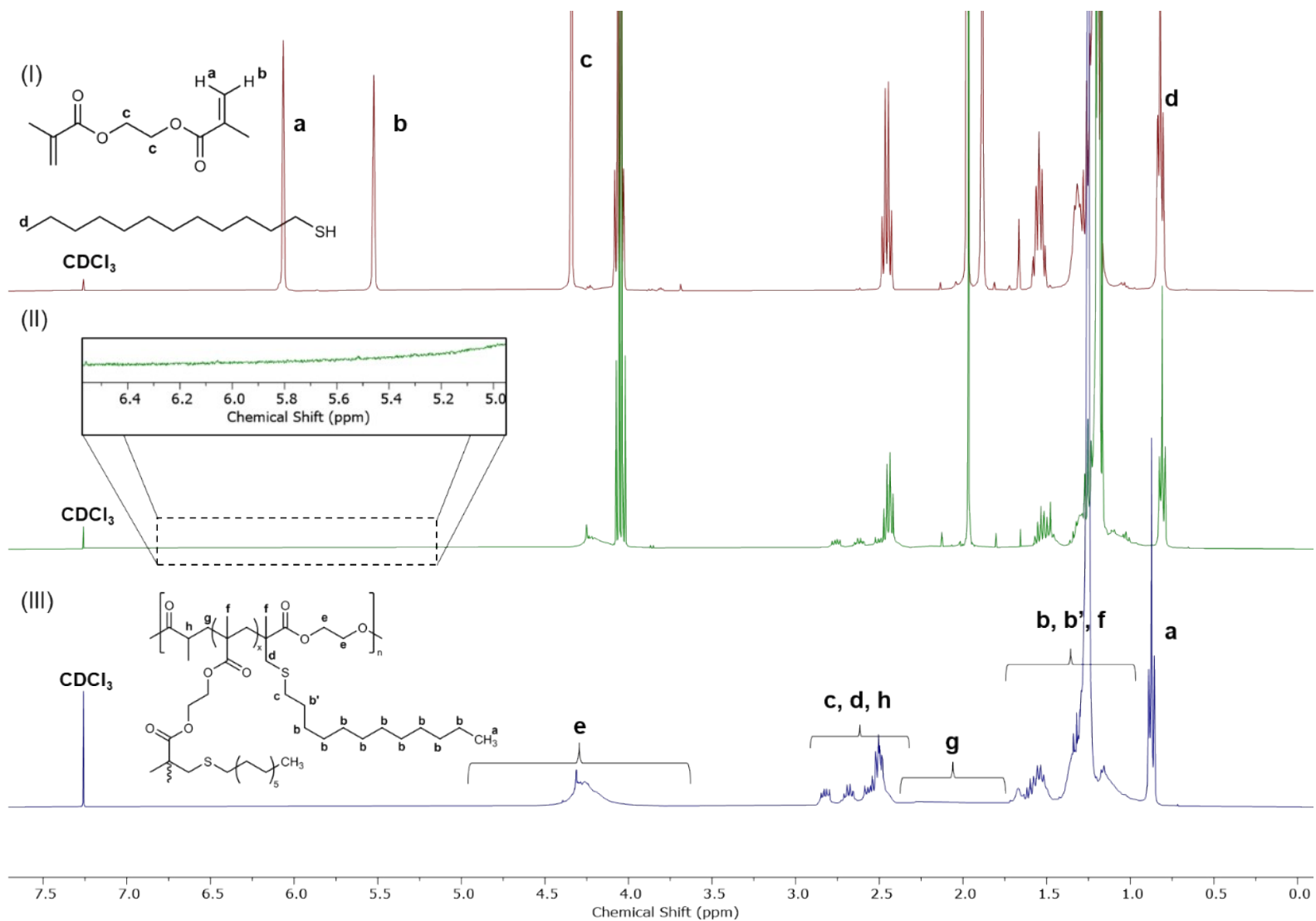


Figure S4 1H NMR spectra (400 MHz, $CDCl_3$) of [EGDMA]/[DDT] conducted at 30 wt% EtOAc. (I) $[EGDMA]_0/[DDT]_0 = 0.650$, (II) the crude sample after 24 hours, and (III) the purified and dried material, $[EGDMA]_F/[DDT]_F = 0.85$.

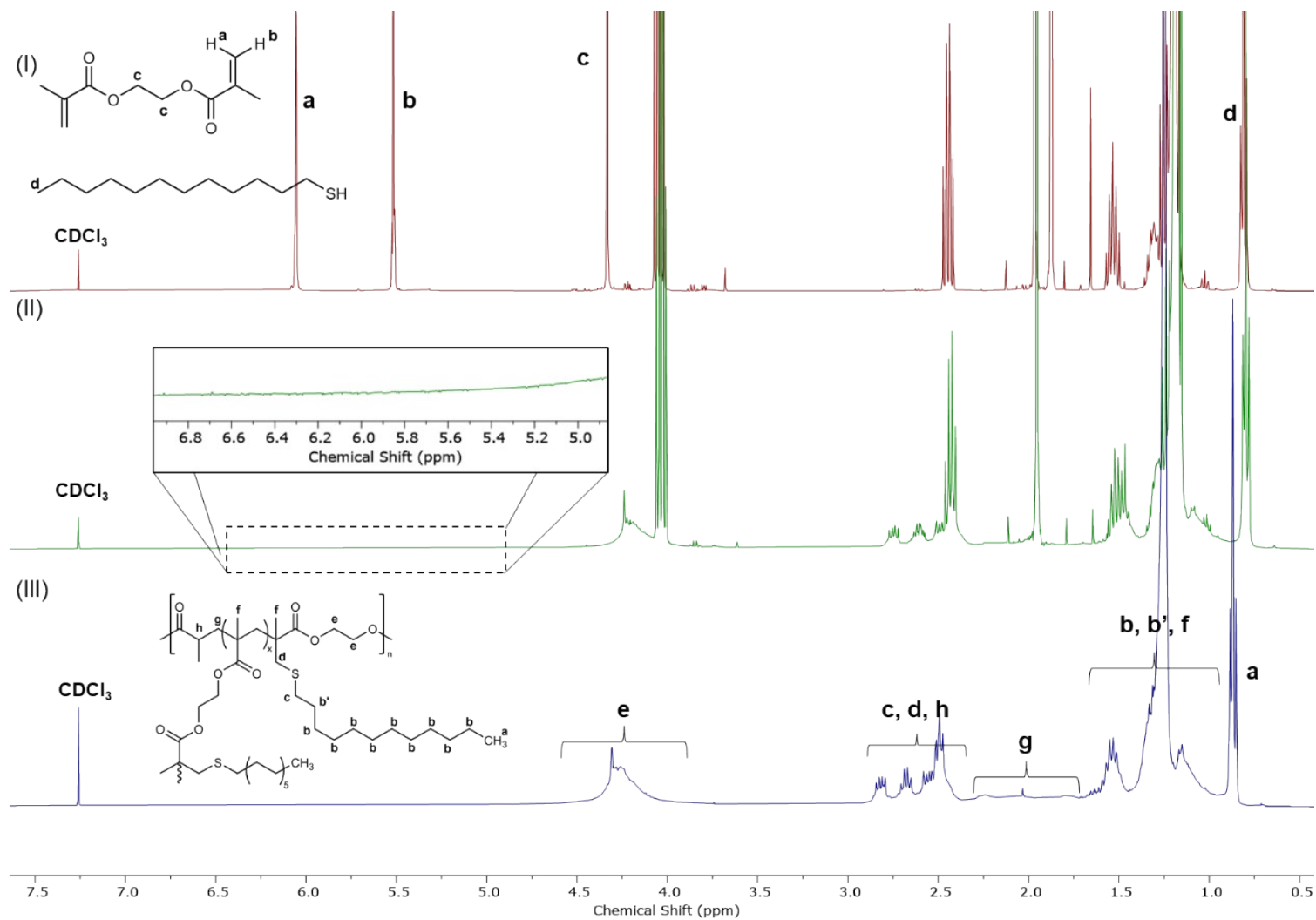


Figure S5 ^1H NMR spectra (400 MHz, CDCl_3) of [EGDMA]/[DDT] conducted at 40 wt% EtOAc. (I) [EGDMA]₀/[DDT]₀ = 0.750, (II) the crude sample after 24 hours, and (III) the purified and dried material, [EGDMA]_x/[DDT]_x = 1.00.

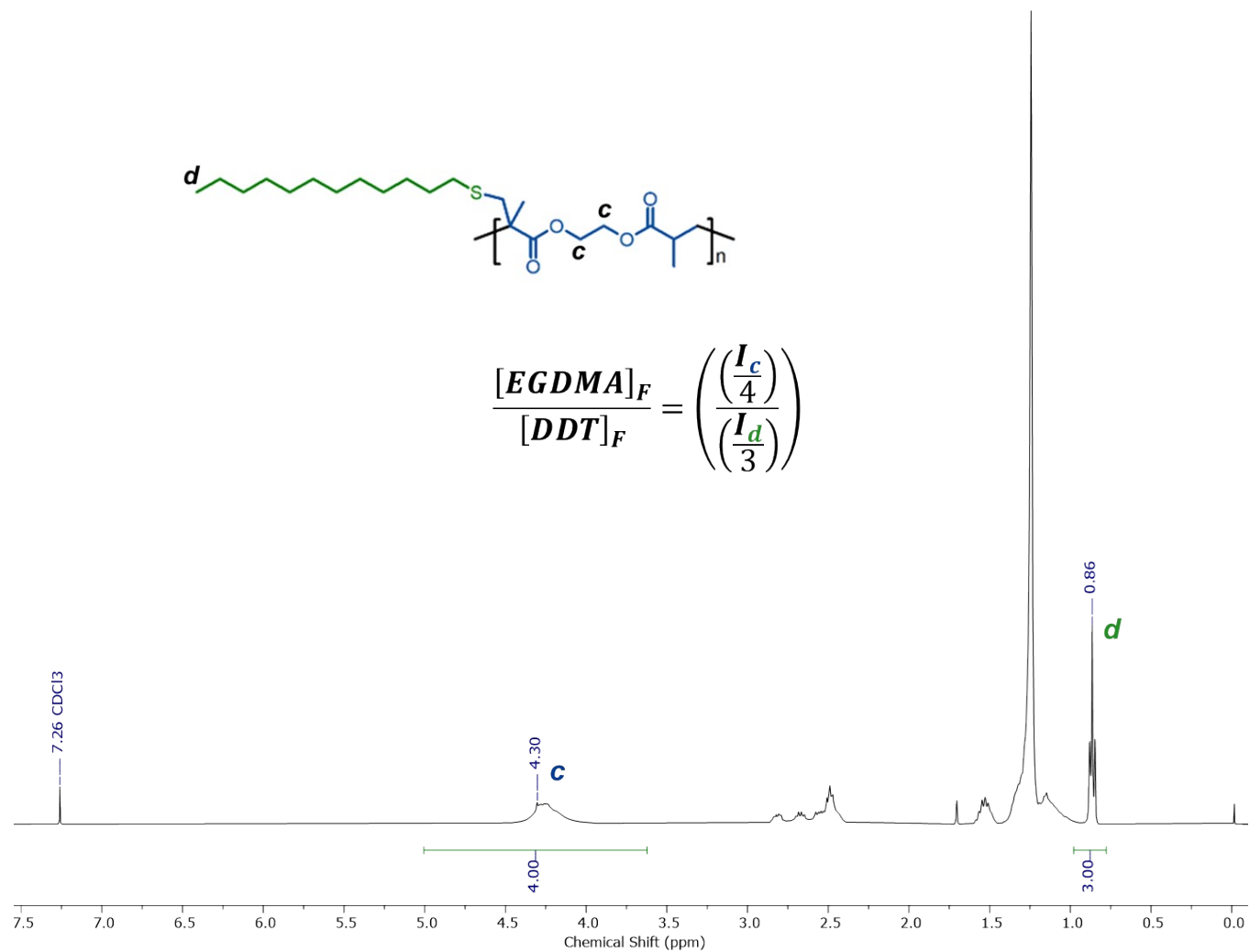


Figure S6 ^1H NMR (400 MHz, CDCl_3) of the purified $[\text{EGDMA}]_0/[\text{DDT}]_0 = 0.850$ reaction generated at 50 wt% EtOAc. Calculation of the ratio of EGMDA to DDT within the purified product based on comparison of the integrals from chemical shifts of EGMDA (*c*, $-\text{CH}_2\text{CH}_2-$, 4.30 ppm) and DDT (*d*, $-\text{CH}_3$, 0.86 ppm), following normalisation of the methyl group on DDT at 0.86 ppm to 3H.

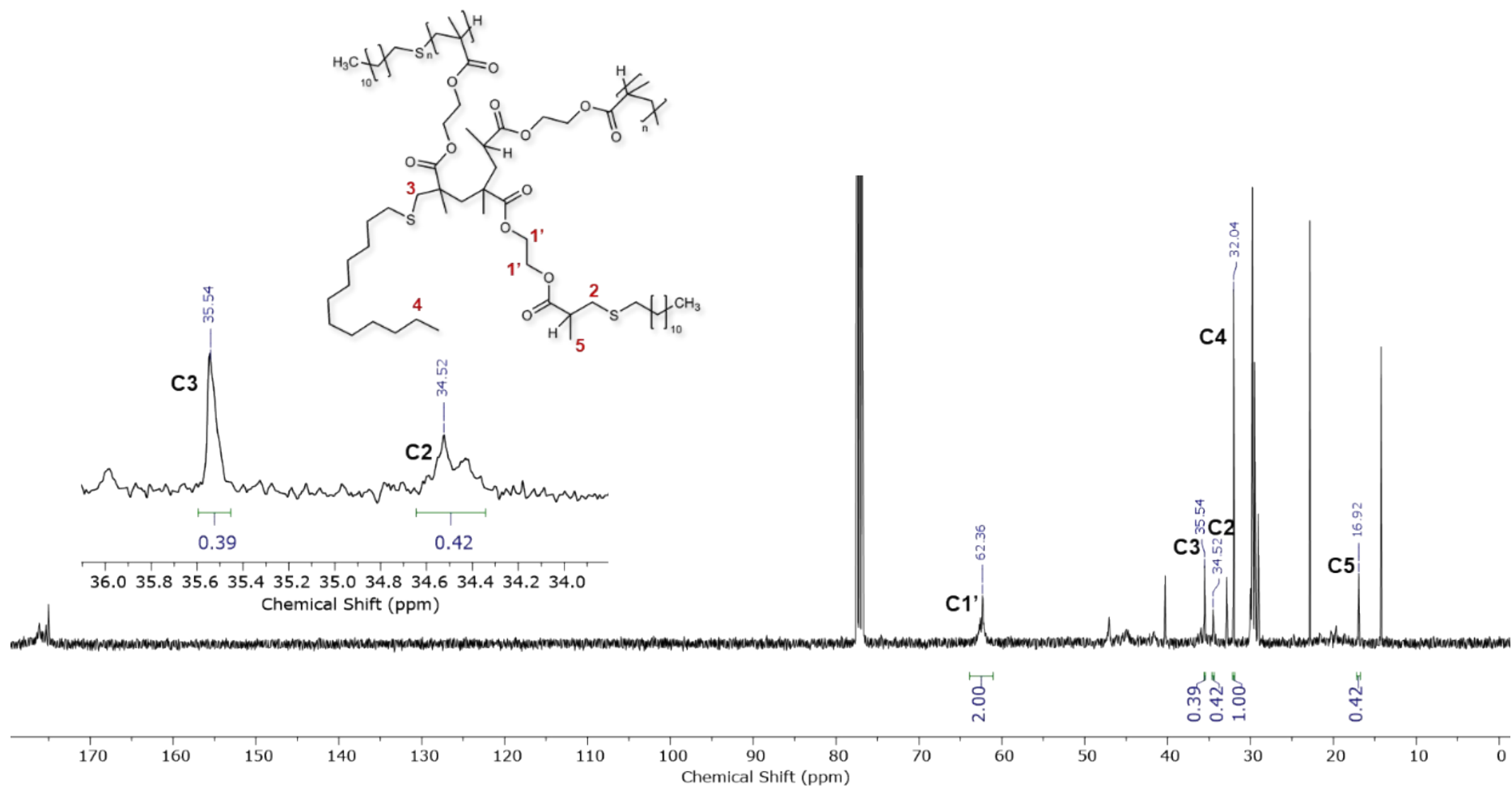


Figure S7 Inverse-gated ^{13}C NMR (100 MHz, CDCl_3) of the purified $[\text{EGDMA}]_0/[\text{DDT}]_0 = 0.450$ reaction generated at 0 wt% EtOAc. Peaks corresponding to the total EGDMA (C1; 62.36 ppm), terminal carbons (C2; 34.52 ppm and C5; 16.92 ppm), linear carbons (C3; 35.54 ppm) and the total DDT (C4; 32.04 ppm) are labelled.

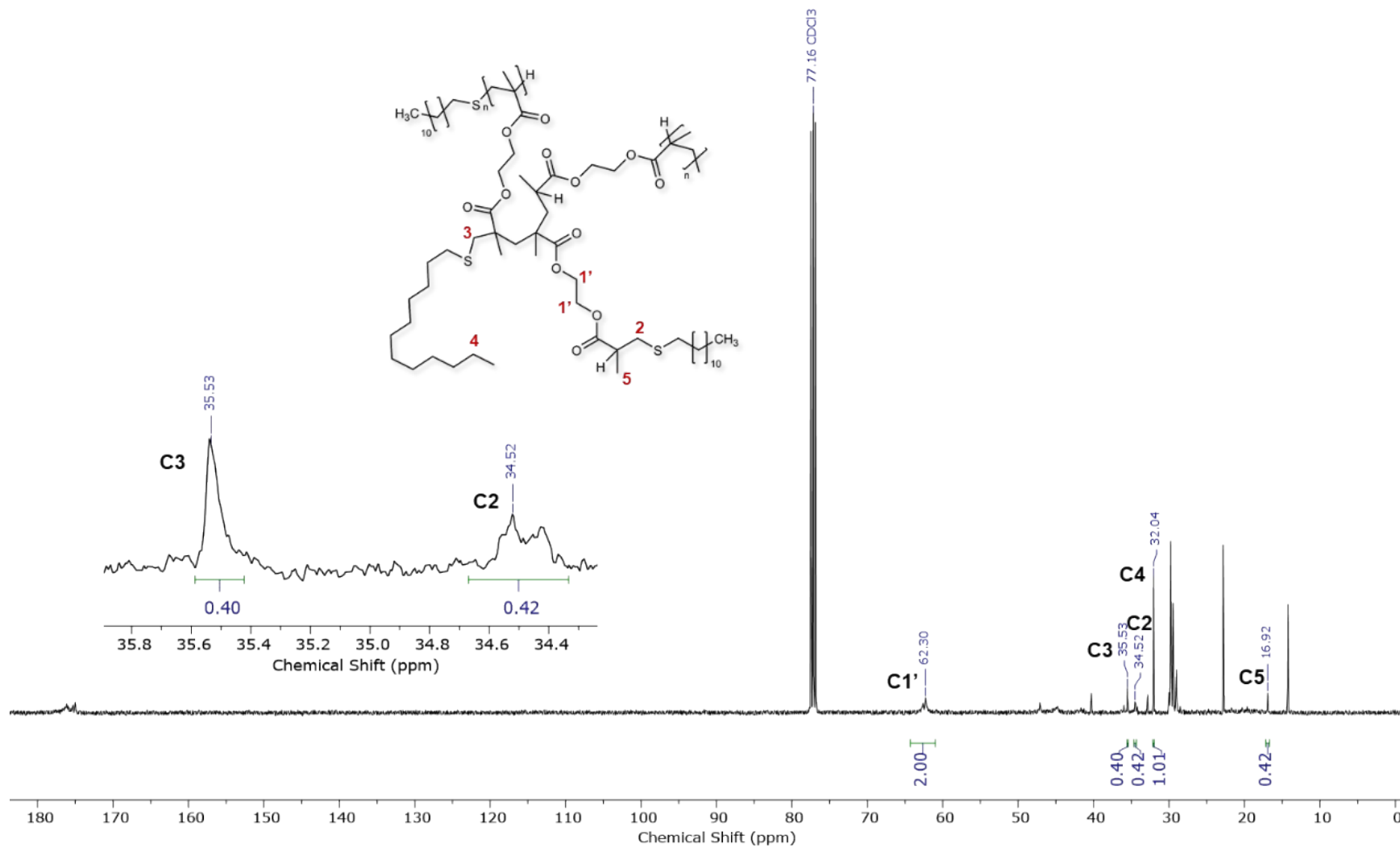


Figure S8 Inverse-gated ¹³C NMR (100 MHz, CDCl₃) of the purified [EGDMA]₀/[DDT]₀ = 0.525 reaction generated at 10 wt% EtOAc. Peaks corresponding to the total EGDMA (C1; 62.30 ppm), terminal carbons (C2; 34.52 ppm and C5; 16.92 ppm), linear carbons (C3; 35.53 ppm) and the total DDT (C4; 32.04 ppm) are labelled.

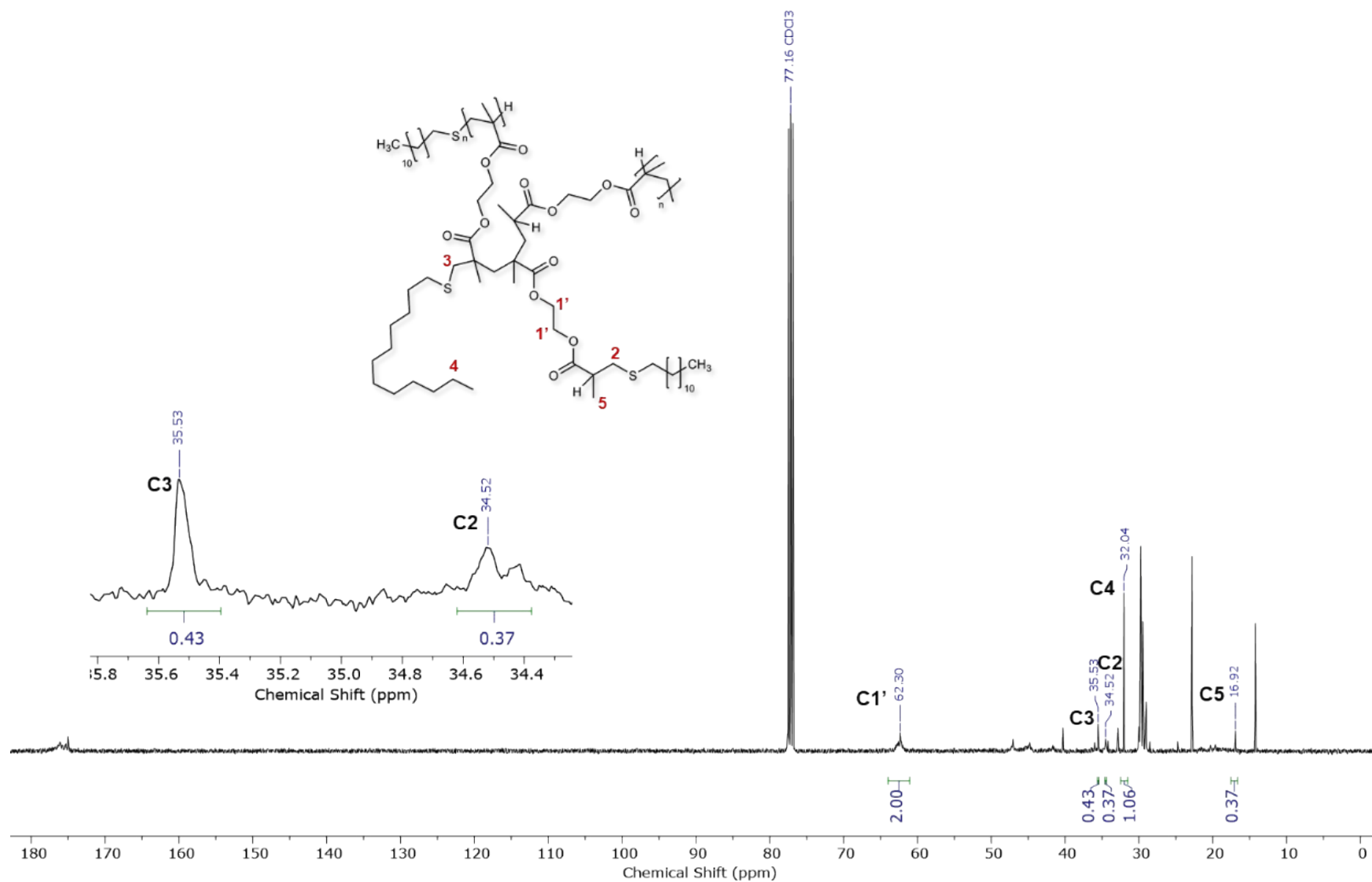


Figure S9 Inverse-gated ^{13}C NMR (100 MHz, CDCl_3) of the purified $[\text{EGDMA}]_0/[\text{DDT}]_0 = 0.600$ reaction generated at 20 wt% EtOAc. Peaks corresponding to the total EGDMA (C1; 62.27 ppm), terminal carbons (C2; 34.51 ppm and C5; 16.92 ppm), linear carbons (C3; 35.51 ppm) and the total DDT (C4; 32.03 ppm) are labelled.

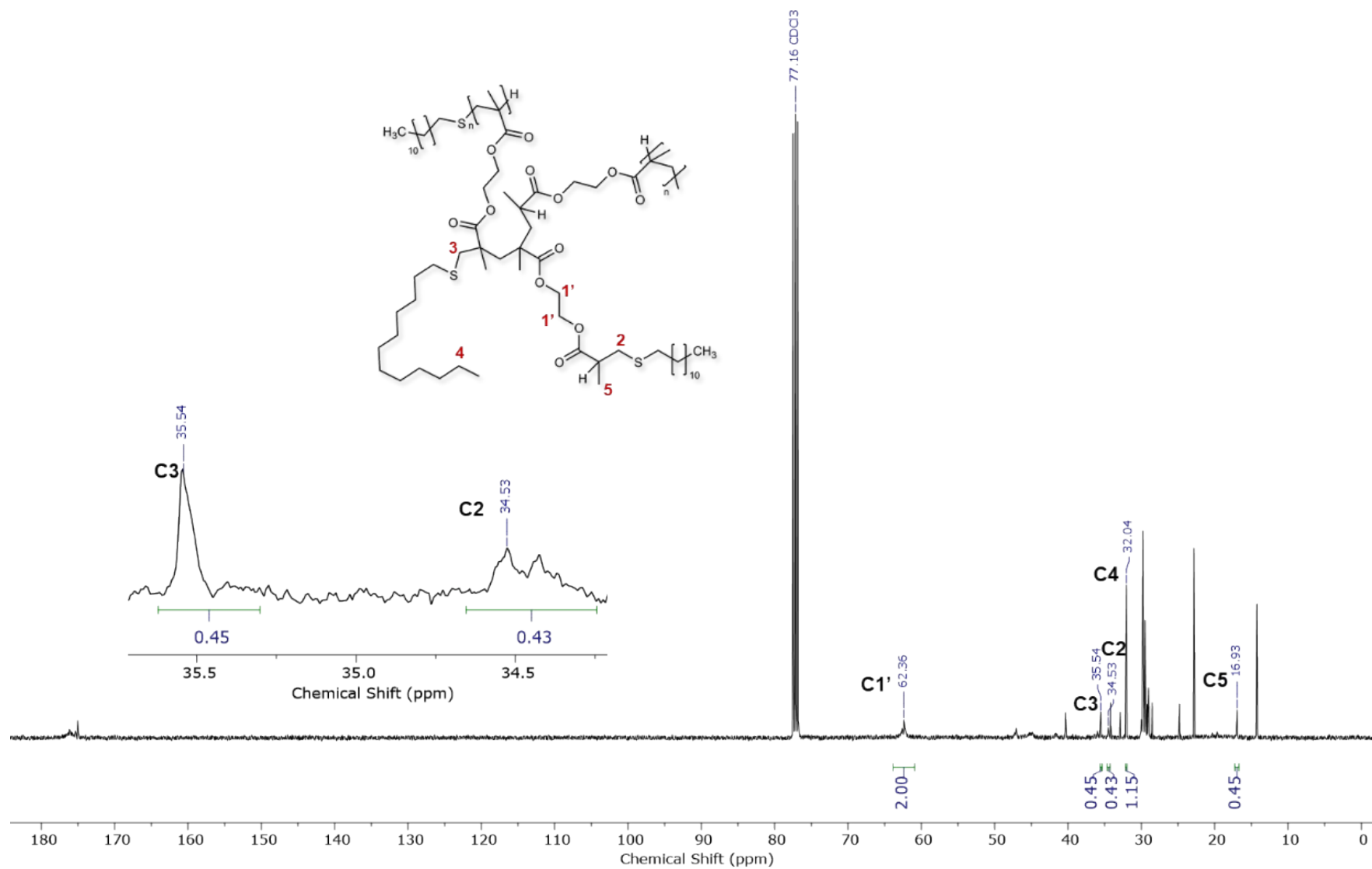


Figure S10 Inverse-gated ^{13}C NMR (100 MHz, CDCl_3) of the purified $[\text{EGDMA}]_0/[\text{DDT}]_0 = 0.650$ reaction generated at 30 wt% EtOAc. Peaks corresponding to the total EGDMA (C1; 62.36 ppm), terminal carbons (C2; 34.53 ppm and C5; 16.93 ppm), linear carbons (C3; 35.41 ppm) and the total DDT (C4; 32.04 ppm) are labelled.

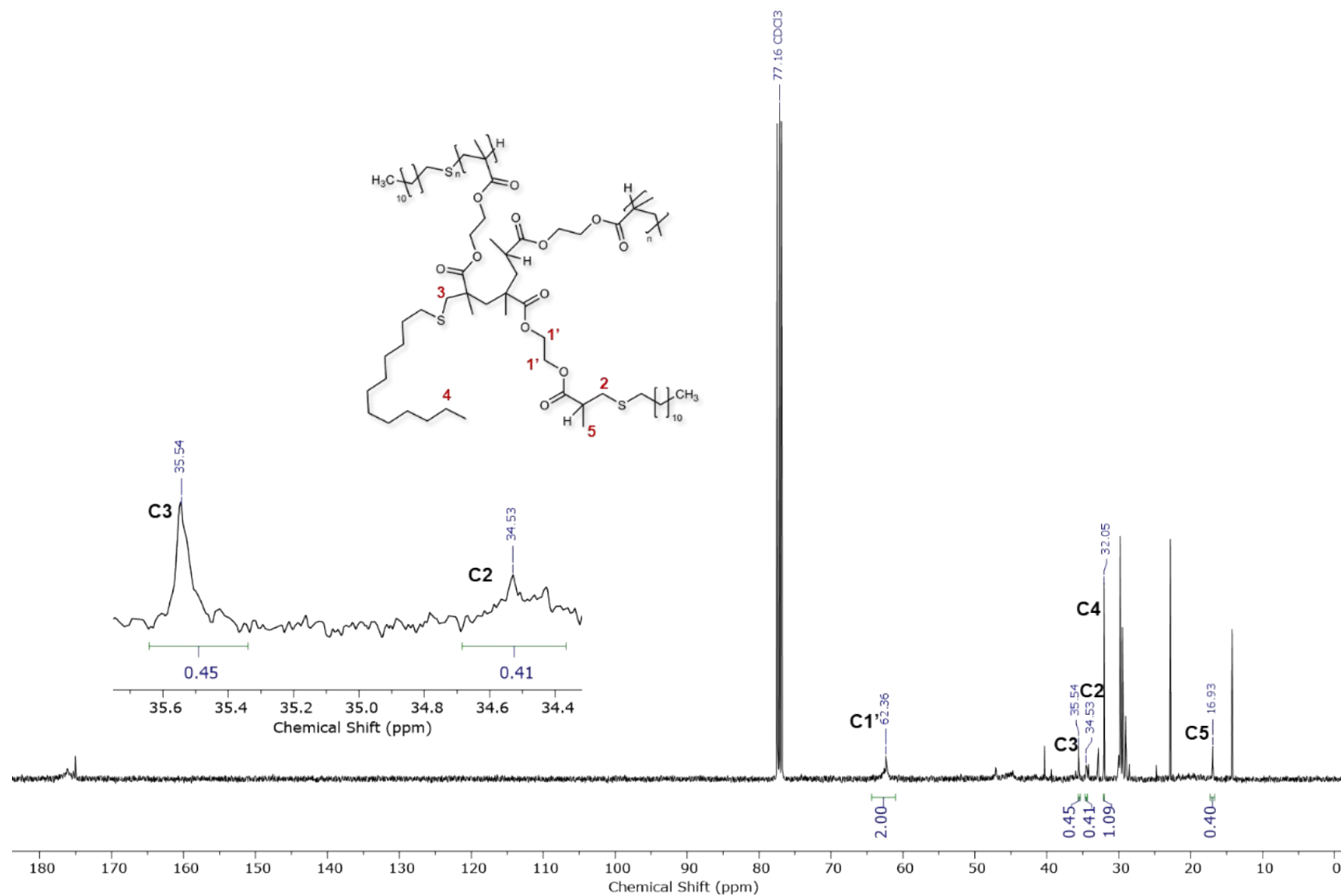


Figure S11 Inverse-gated ¹³C NMR (100 MHz, CDCl₃) of the purified [EGDMA]₀/[DDT]₀ = 0.750 reaction generated at 40 wt% EtOAc. Peaks corresponding to the total EGDMA (C1; 62.36 ppm), terminal carbons (C2; 34.53 ppm and C5; 16.93 ppm), linear carbons (C3; 35.54 ppm) and the total DDT (C4; 32.05 ppm) are labelled.

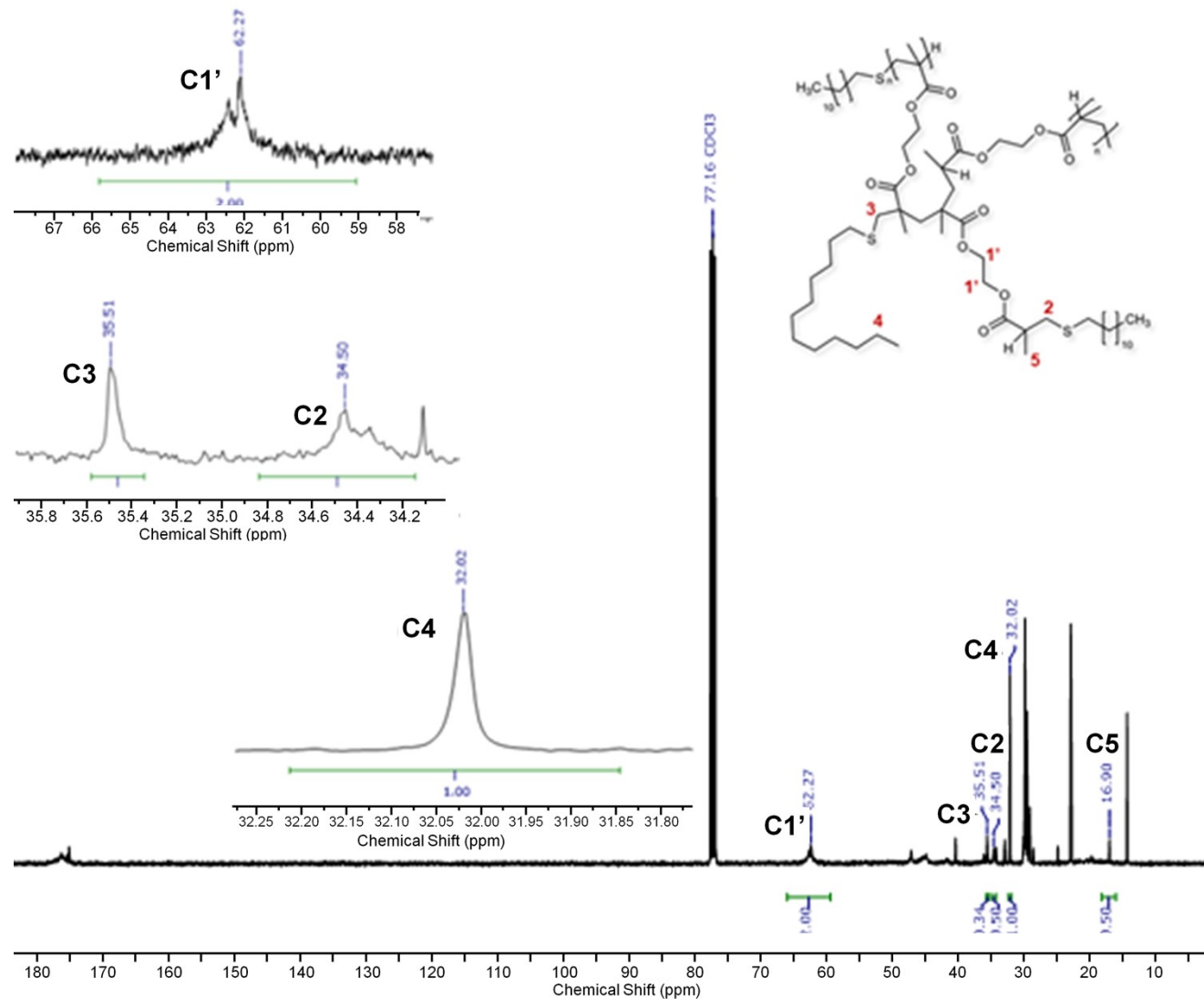


Figure S12 Inverse-gated ^{13}C NMR (100 MHz, CDCl_3) of the purified $[\text{EGDMA}]_0/[\text{DDT}]_0 = 0.850$ reaction generated at 50 wt% EtOAc. Peaks corresponding to the total EGDMA (C1; 62.27 ppm), terminal carbons (C2; 34.50 ppm and C5; 16.90 ppm), linear carbons (C3; 35.51 ppm) and the total DDT (C4; 32.02 ppm) are labelled.

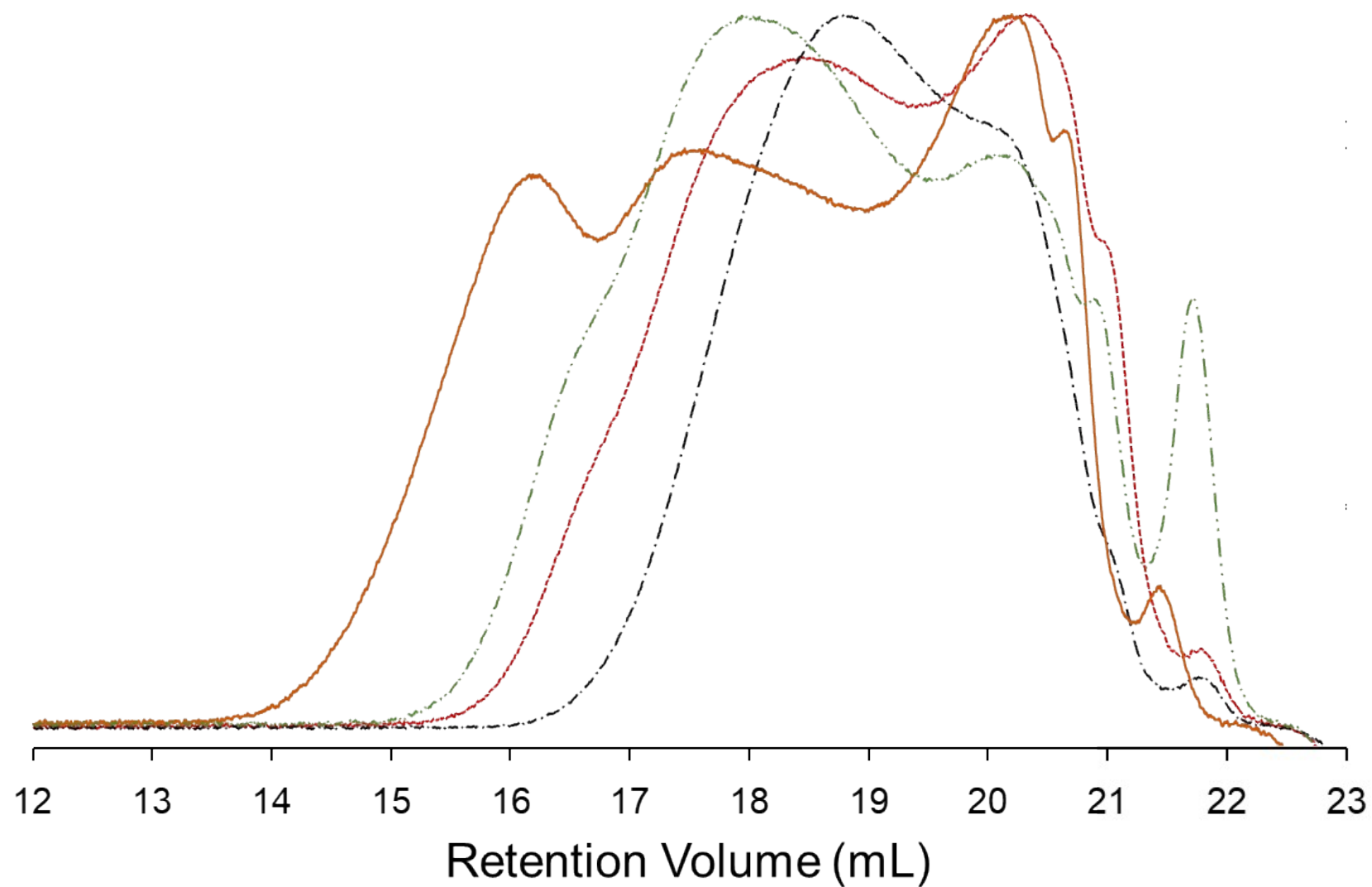


Figure S13 TD-SEC (THF eluent; refractive index (RI) detector signal) showing the molecular weight distributions of branched polymers derived from the $[\text{EGDMA}]_0/[\text{DDT}]_0$ at various EGDMA:DDT ratios conducted at 0 wt% EtOAc. The overlaid chromatograms show of the distribution of $[\text{EGDMA}]_0/[\text{DDT}]_0 = 0.350$ (black dash dot line), 0.400 (red square dot line), 0.425 (green dash dot dot line) and 0.450 (orange solid line) ratios.

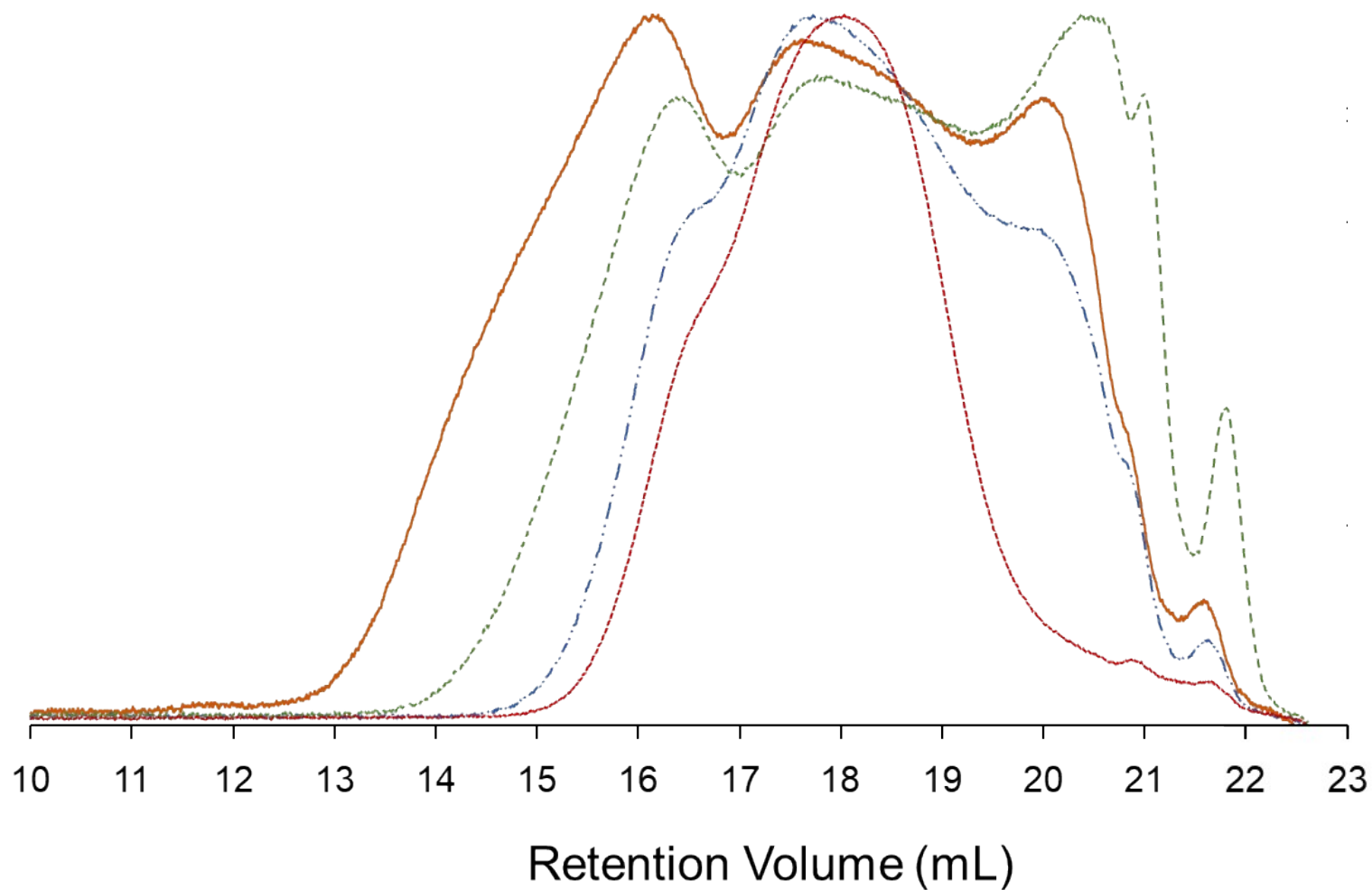


Figure S14 TD-SEC (THF eluent; refractive index (RI) detector signal) showing the molecular weight distributions of branched polymers derived from the $[\text{EGDMA}]_0/[\text{DDT}]_0$ at various EGDMA:DDT ratios conducted at 10 wt% solvent. The overlaid chromatograms show of the distribution of $[\text{EGDMA}]_0/[\text{DDT}]_0 = 0.450$ (red square dot line), 0.475 (blue dash dot dot line), 0.500 (green dash line) and 0.525 (orange solid line) ratios.

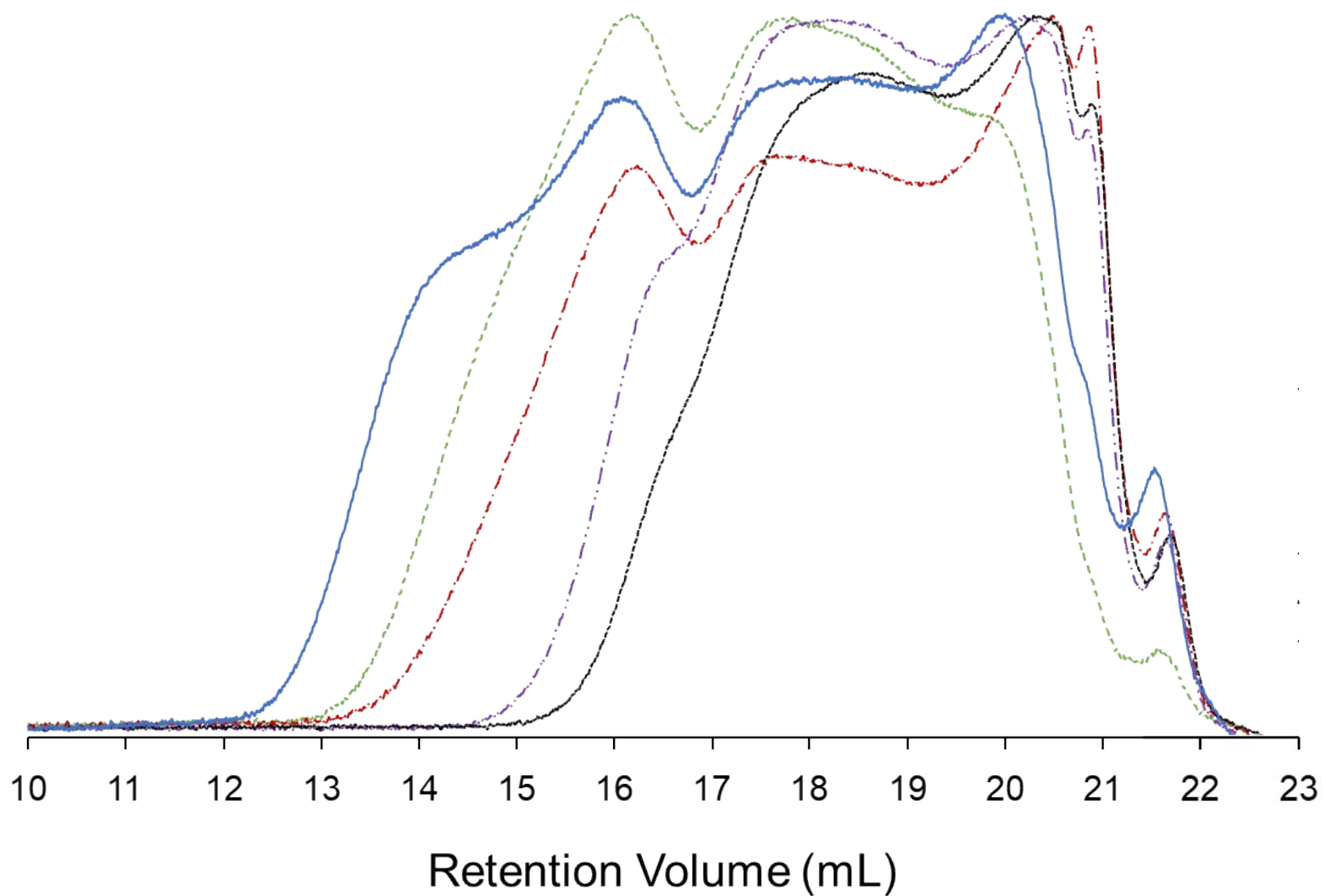


Figure S15 TD-SEC (THF eluent; refractive index (RI) detector signal) showing the molecular weight distributions of branched polymers derived from the $[\text{EGDMA}]_0/[\text{DDT}]_0$ at various EGDMA:DDT ratios conducted at 20 wt% solvent. The overlaid chromatograms show of the distribution of $[\text{EGDMA}]_0/[\text{DDT}]_0 = 0.500$ (black square dot line), 0.525 (purple dash dot dot line), 0.550 (red dash dot line), 0.575 (green dash line) and 0.600 (blue solid line) ratios.

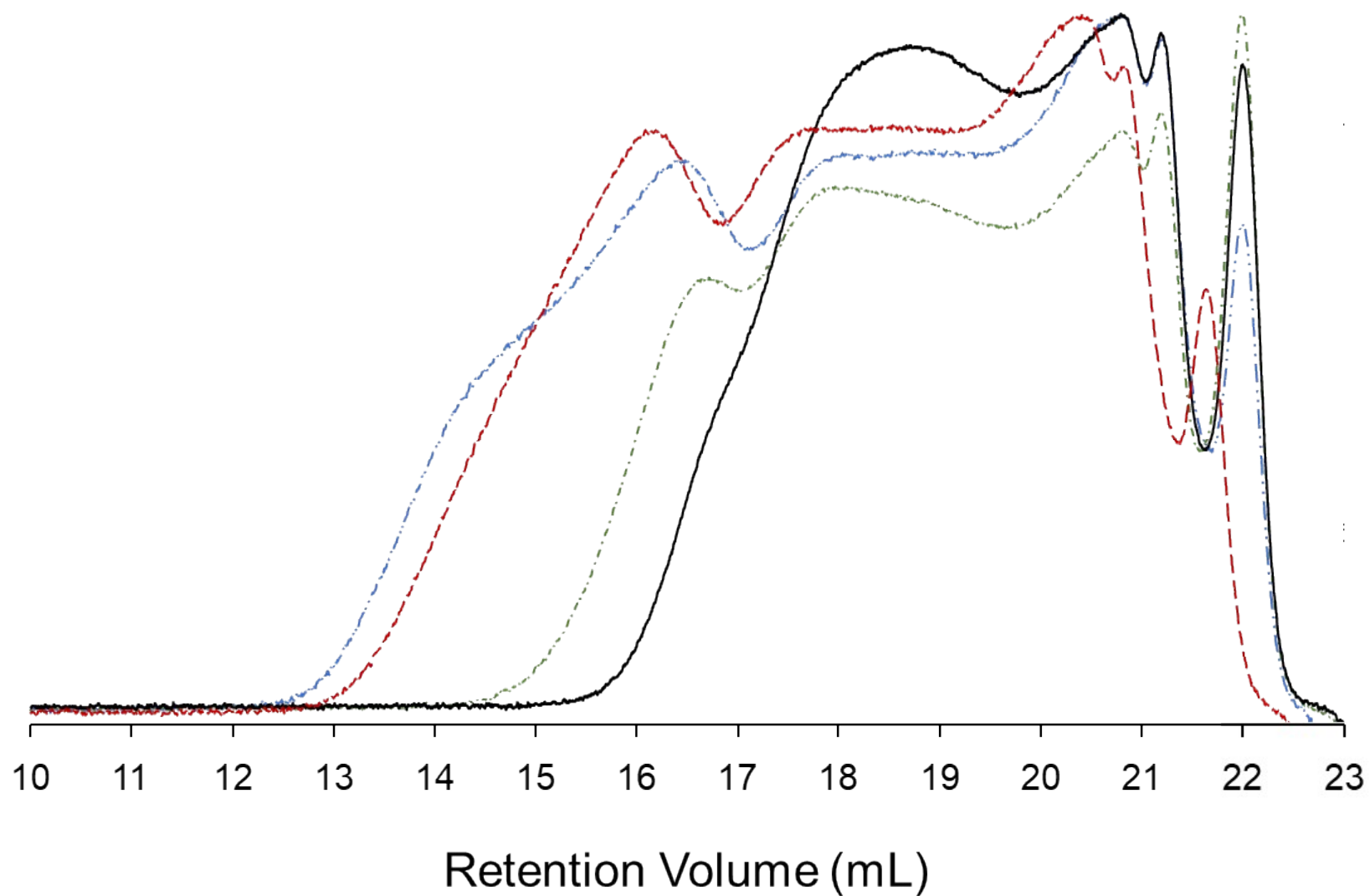


Figure S16 TD-SEC (THF eluent; refractive index (RI) detector signal) showing the molecular weight distributions of branched polymers derived from the $[\text{EGDMA}]_0/[\text{DDT}]_0$ at various EGDMA:DDT ratios conducted at 30 wt% solvent. The overlaid chromatograms show of the distribution of $[\text{EGDMA}]_0/[\text{DDT}]_0 = 0.550$ (black solid line), 0.600 (green dash dot line), 0.620 (red dashed line) and 0.650 (blue dash dot dot line) ratios.

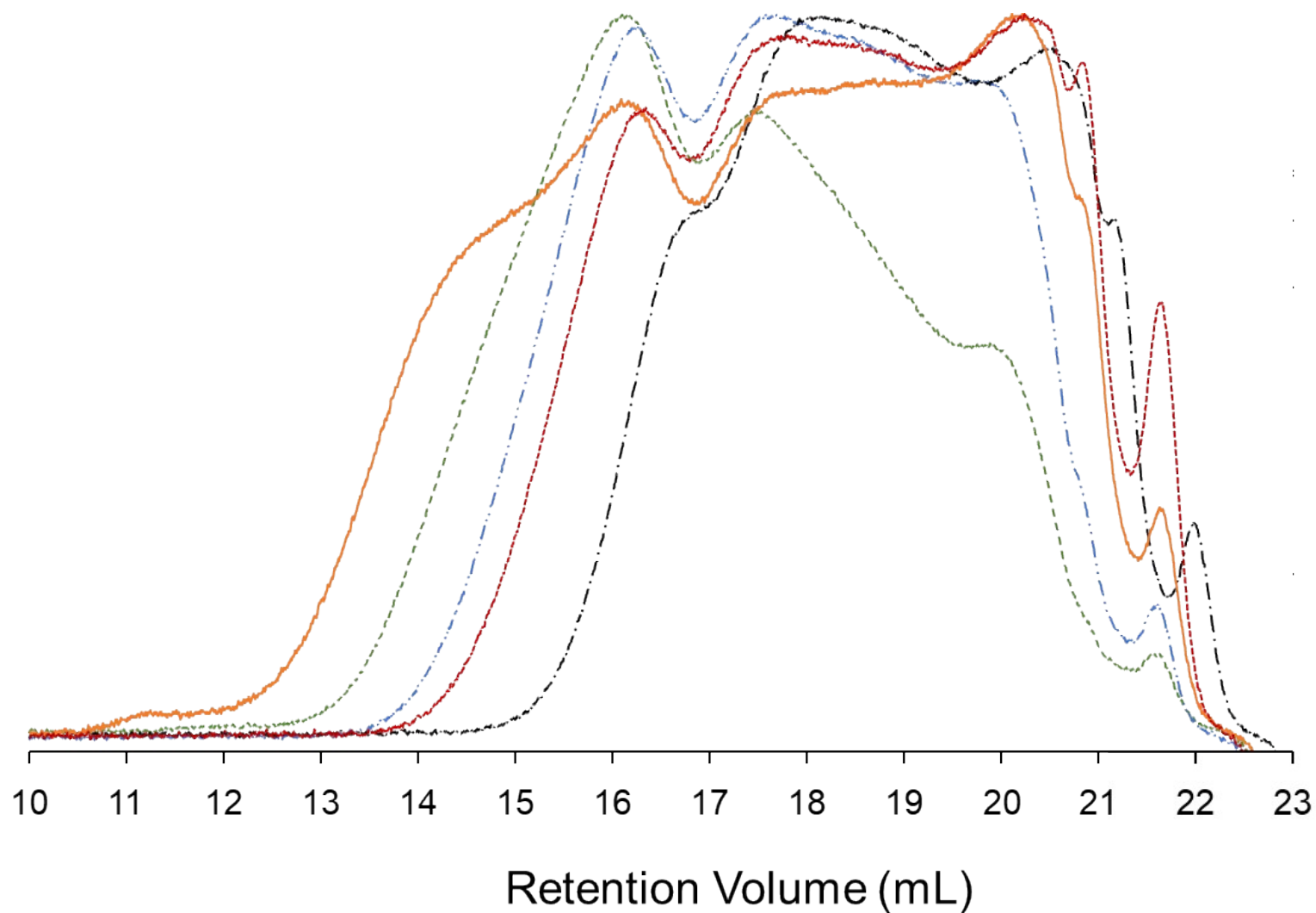


Figure S17 TD-SEC (THF eluent; refractive index (RI) detector signal) showing the molecular weight distributions of branched polymers derived from the $[\text{EGDMA}]_0/[\text{DDT}]_0$ at various EGDMA:DDT ratios conducted at 40 wt% solvent. The overlaid chromatograms show of the distribution of $[\text{EGDMA}]_0/[\text{DDT}]_0 = 0.650$ (black dash dot line), 0.675 (red square dot line), 0.700 (blue dash dot dot line), 0.750 (green dashed line) and 0.725 (orange solid line) ratios.

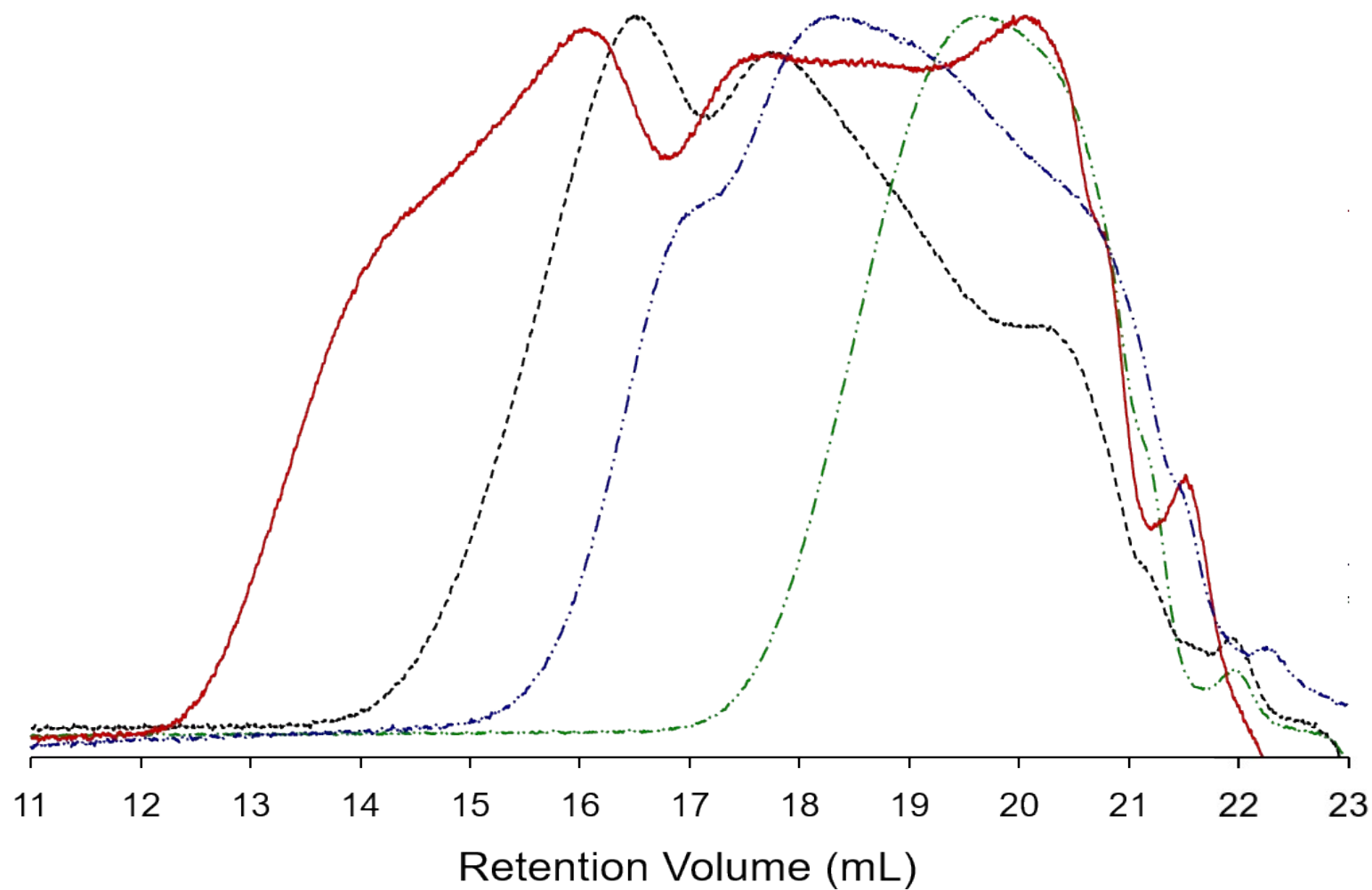


Figure S18 TD-SEC (THF eluent; refractive index (RI) detector signal) showing the molecular weight distributions of branched polymers derived from the $[\text{EGDMA}]_0/[\text{DDT}]_0$ at various EGDMA:DDT ratios conducted at 50 wt% solvent. The overlaid chromatograms show of the distribution of $[\text{EGDMA}]_0/[\text{DDT}]_0 = 0.500$ (green dash dot dot line), 0.750 (blue dash dot dot line), 0.800 (black dash line) and 0.850 (red solid line) ratios.

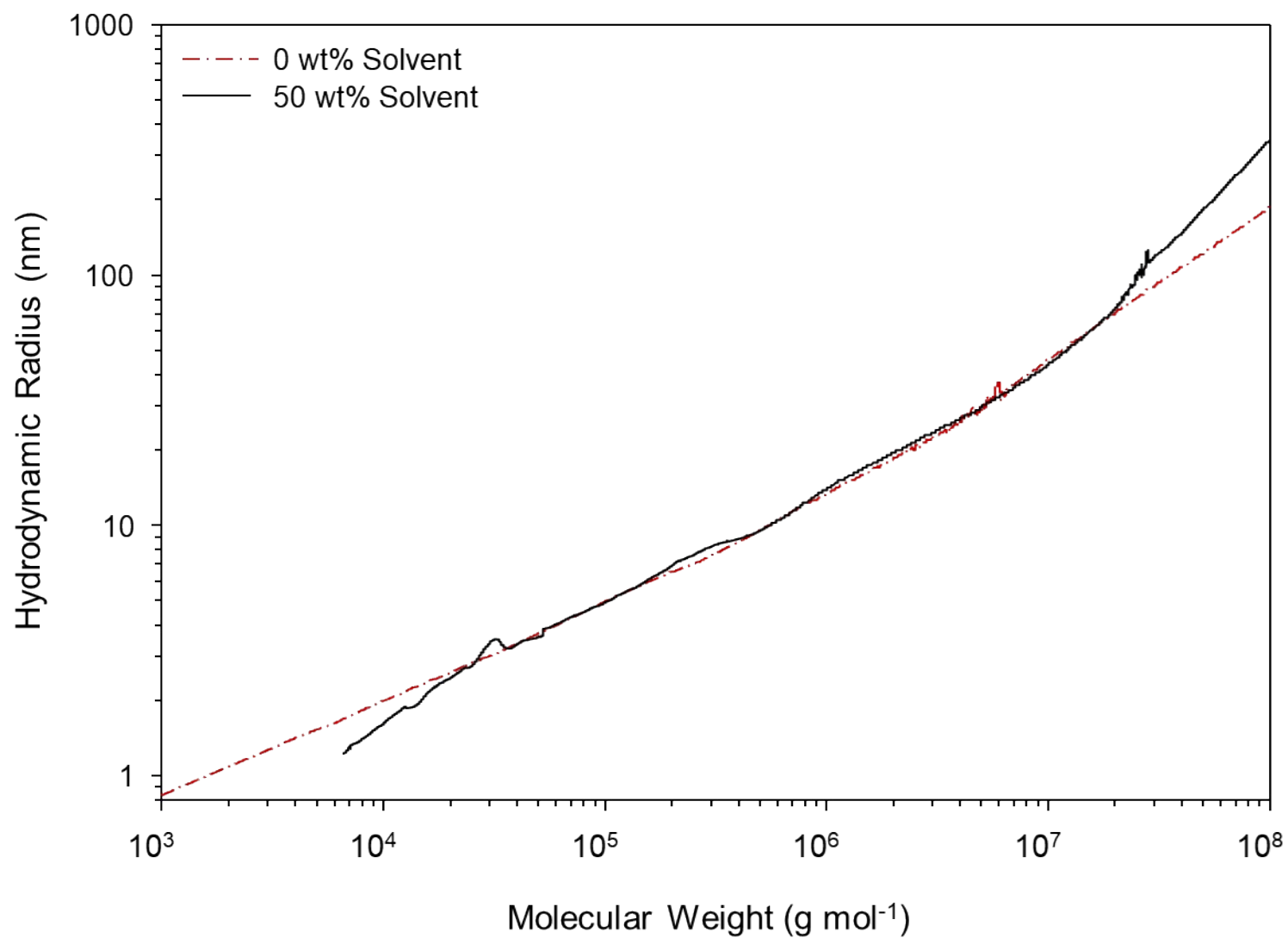


Figure S19 TD-SEC derived analysis of the hydrodynamic radius across the molecular weight distributions for branched polymers generated at 0 wt% solvent (red dash dot line) and 50 wt% solvent (black solid line).

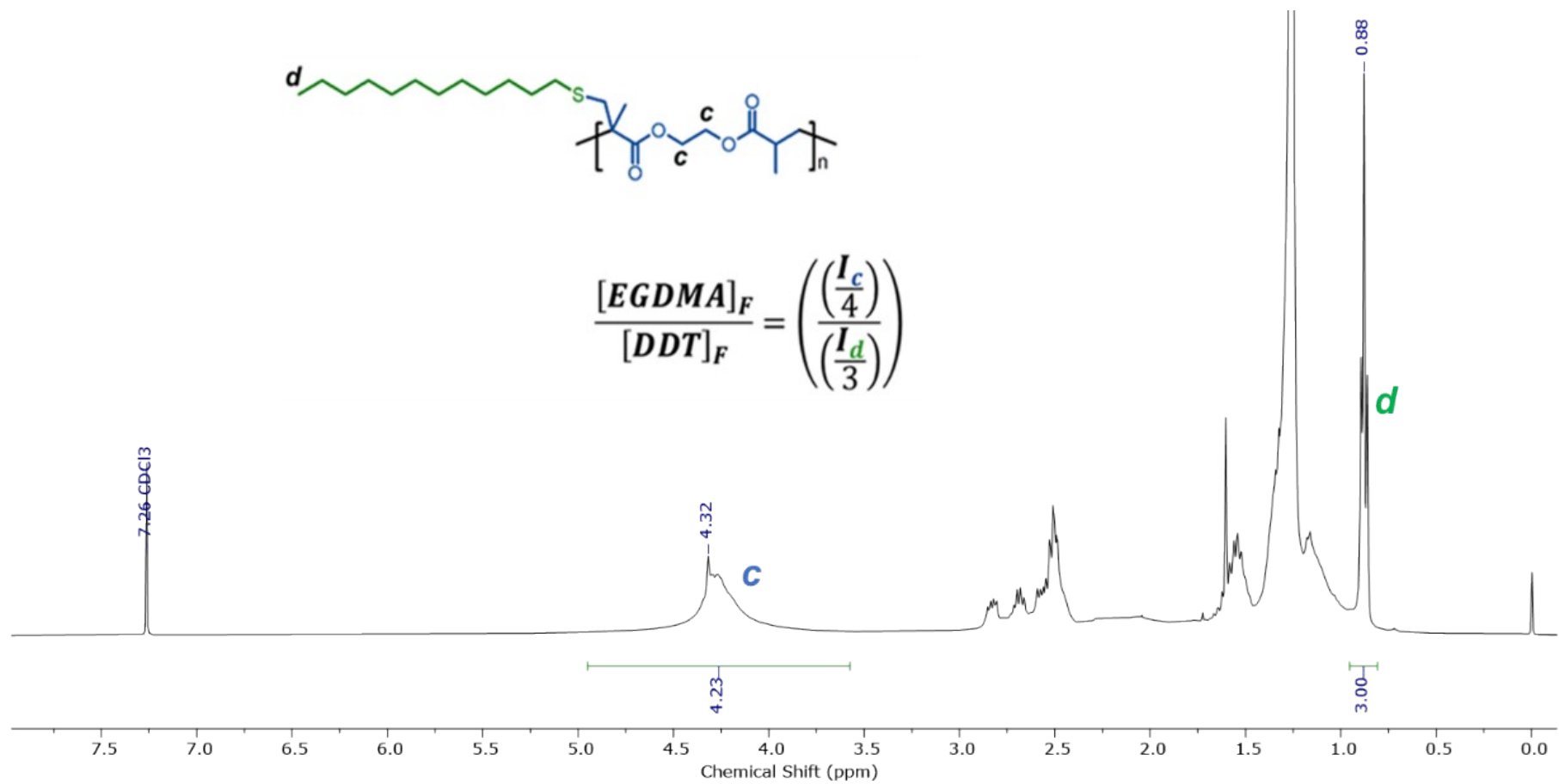


Figure S20 ¹H NMR spectrum (400 MHz, CDCl₃) of the purified and dried material generated at [EGDMA]₀/[DDT]₀ = 1.00 in 60 wt% EtOAc, showing a [EGDMA]_f/[DDT]_f = 1.06.

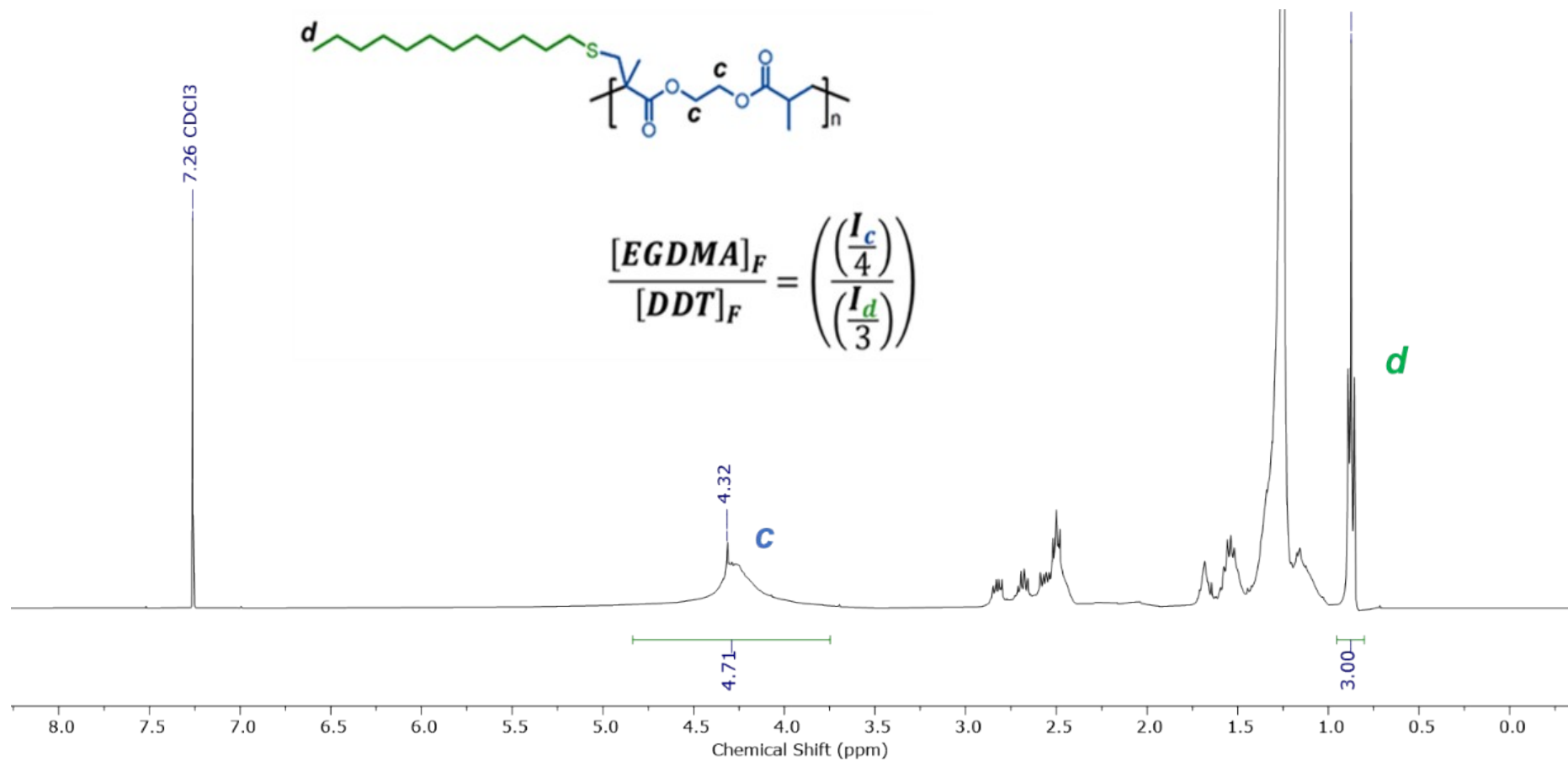
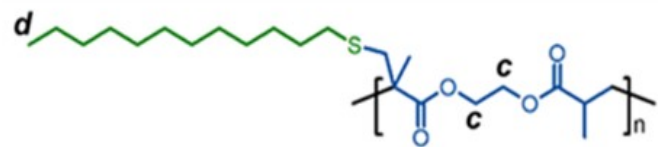


Figure S21 ¹H NMR spectrum (400 MHz, CDCl₃) of the purified and dried material generated at [EGDMA]₀/[DDT]₀ = 1.18 in 70 wt% EtOAc, showing a [EGDMA]_f/[DDT]_f = 1.18.



$$\frac{[EGDMA]_F}{[DDT]_F} = \left(\frac{\left(\frac{I_c}{4} \right)}{\left(\frac{I_d}{3} \right)} \right)$$

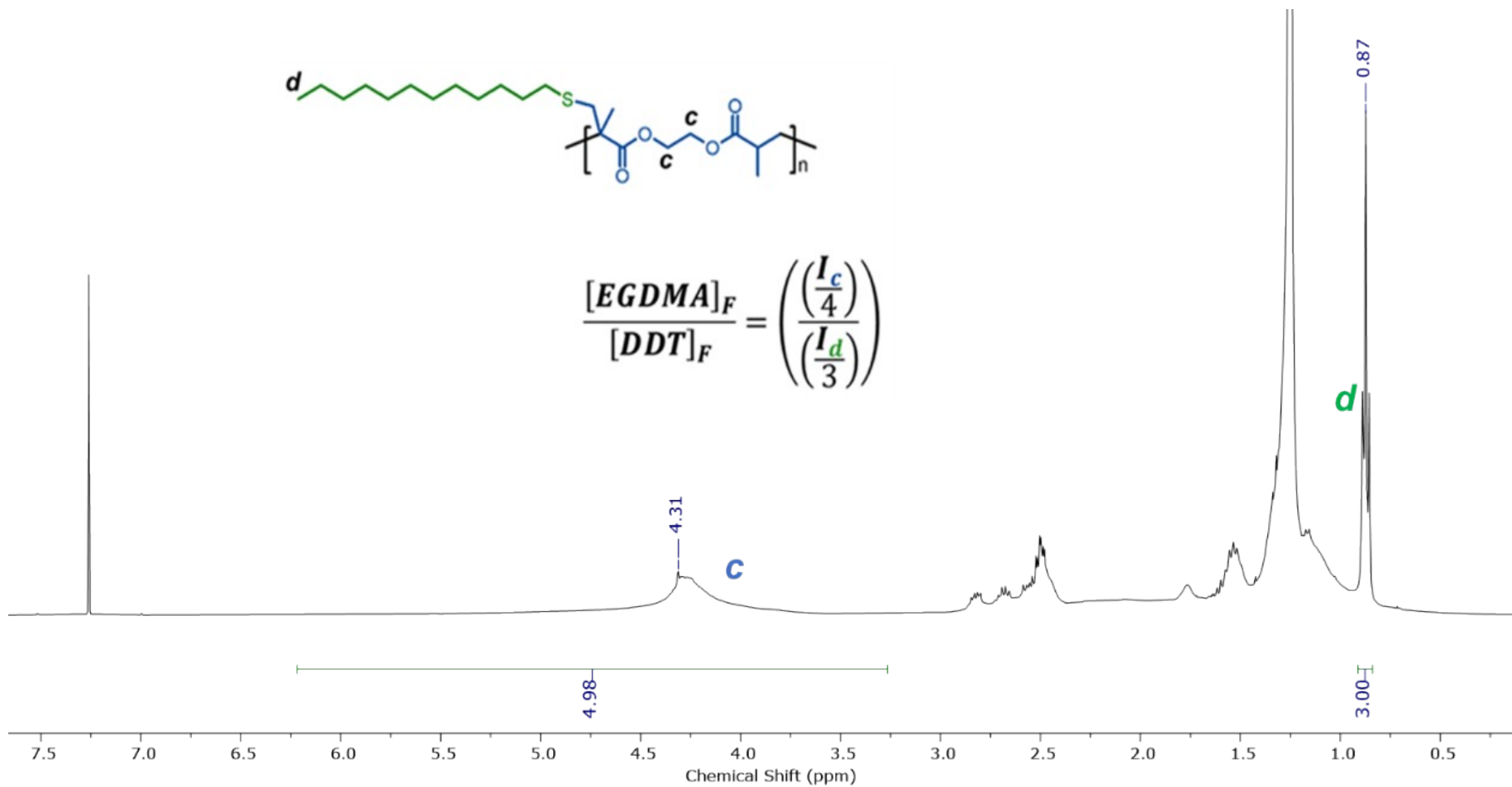


Figure S22 ^1H NMR spectrum (400 MHz, CDCl_3) of the purified and dried material generated at $[\text{EGDMA}]_0/[\text{DDT}]_0 = 1.43$ in 80 wt% EtOAc, showing a $[\text{EGDMA}]_f/[\text{DDT}]_f = 1.25$.

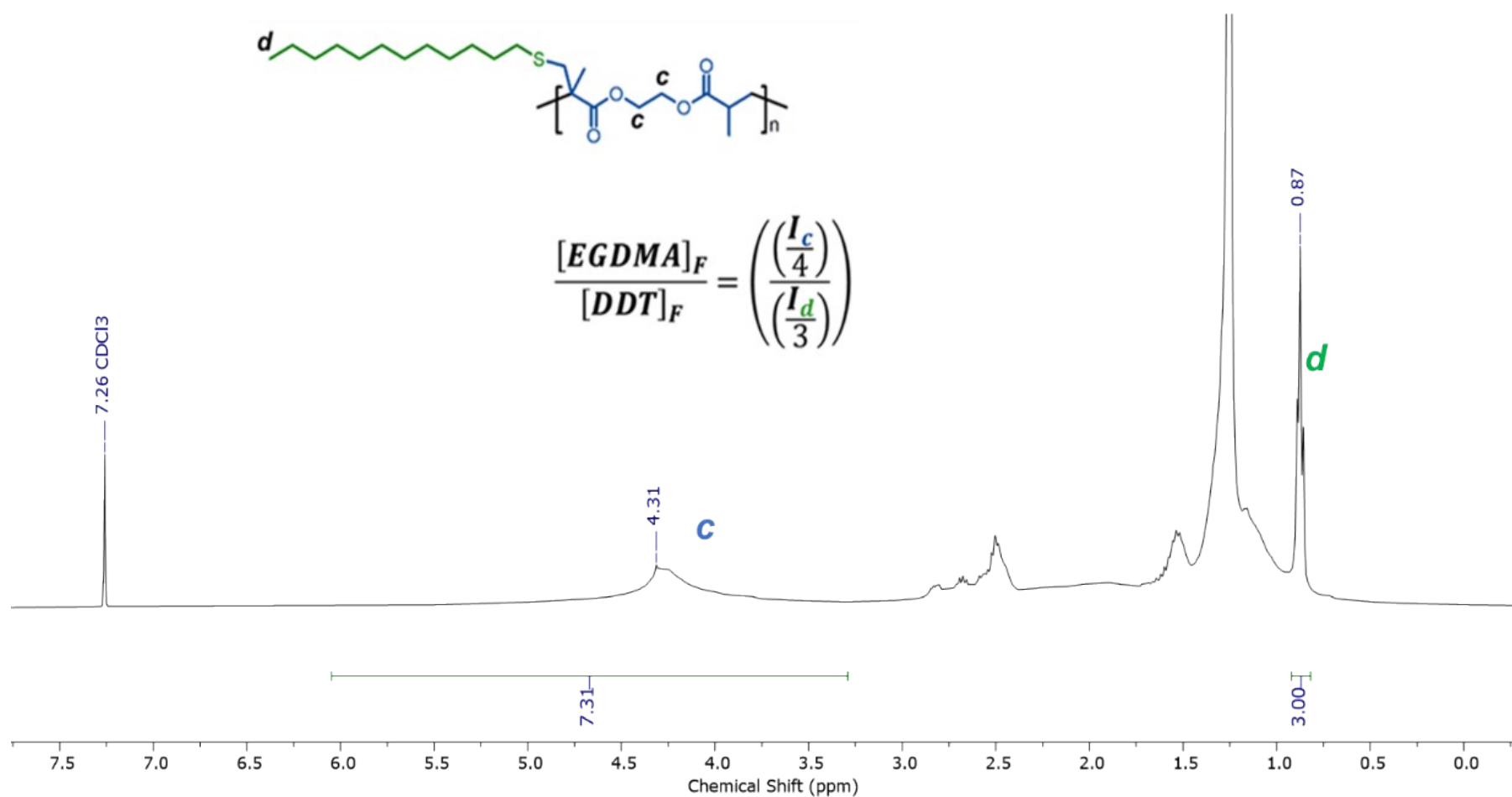


Figure S23 ^1H NMR spectrum (400 MHz, CDCl_3) of the purified and dried material generated at $[\text{EGDMA}]_0/[\text{DDT}]_0 = 2.10$ in 90 wt% EtOAc, showing a $[\text{EGDMA}]_f/[\text{DDT}]_f = 1.83$.

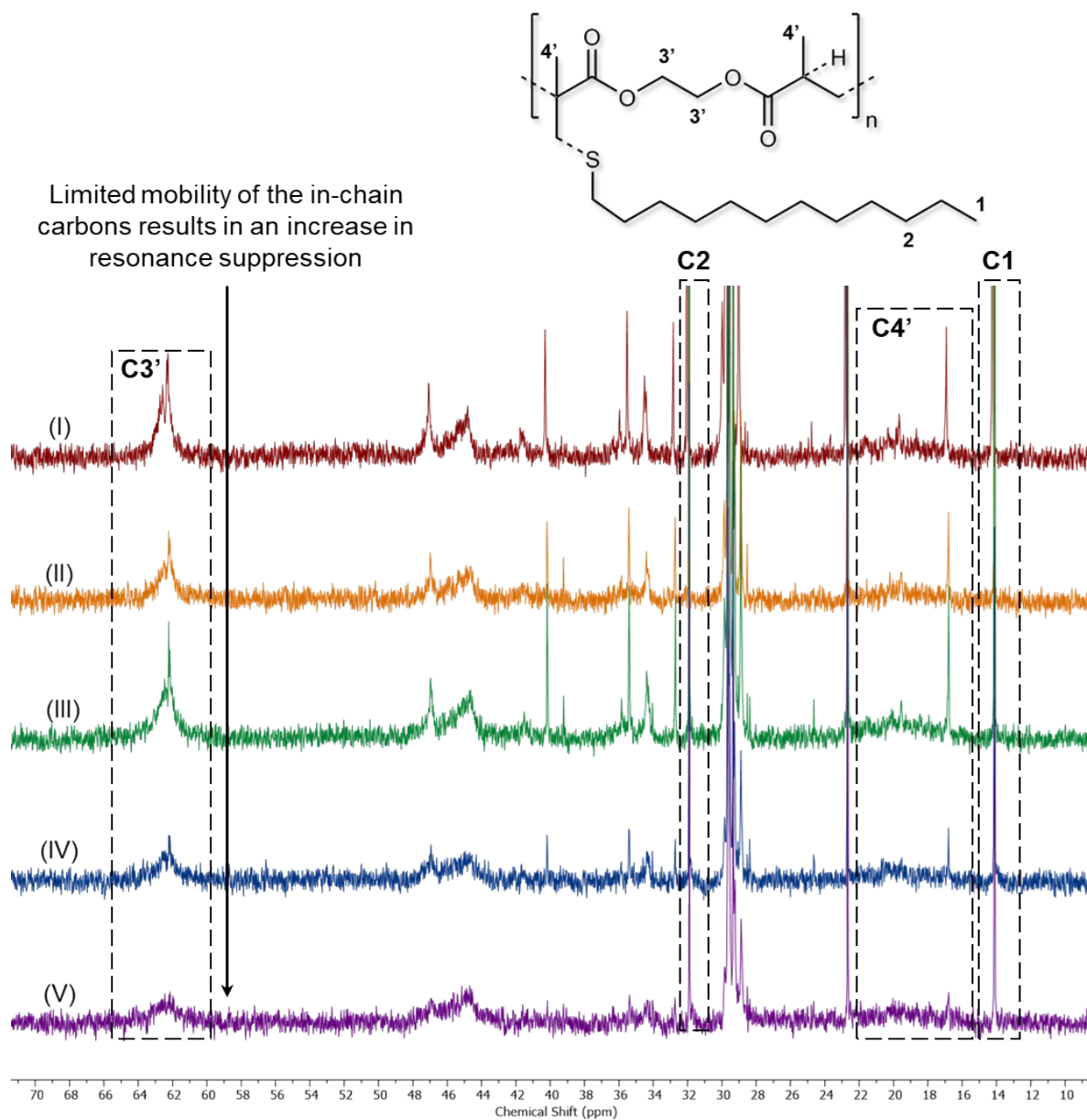
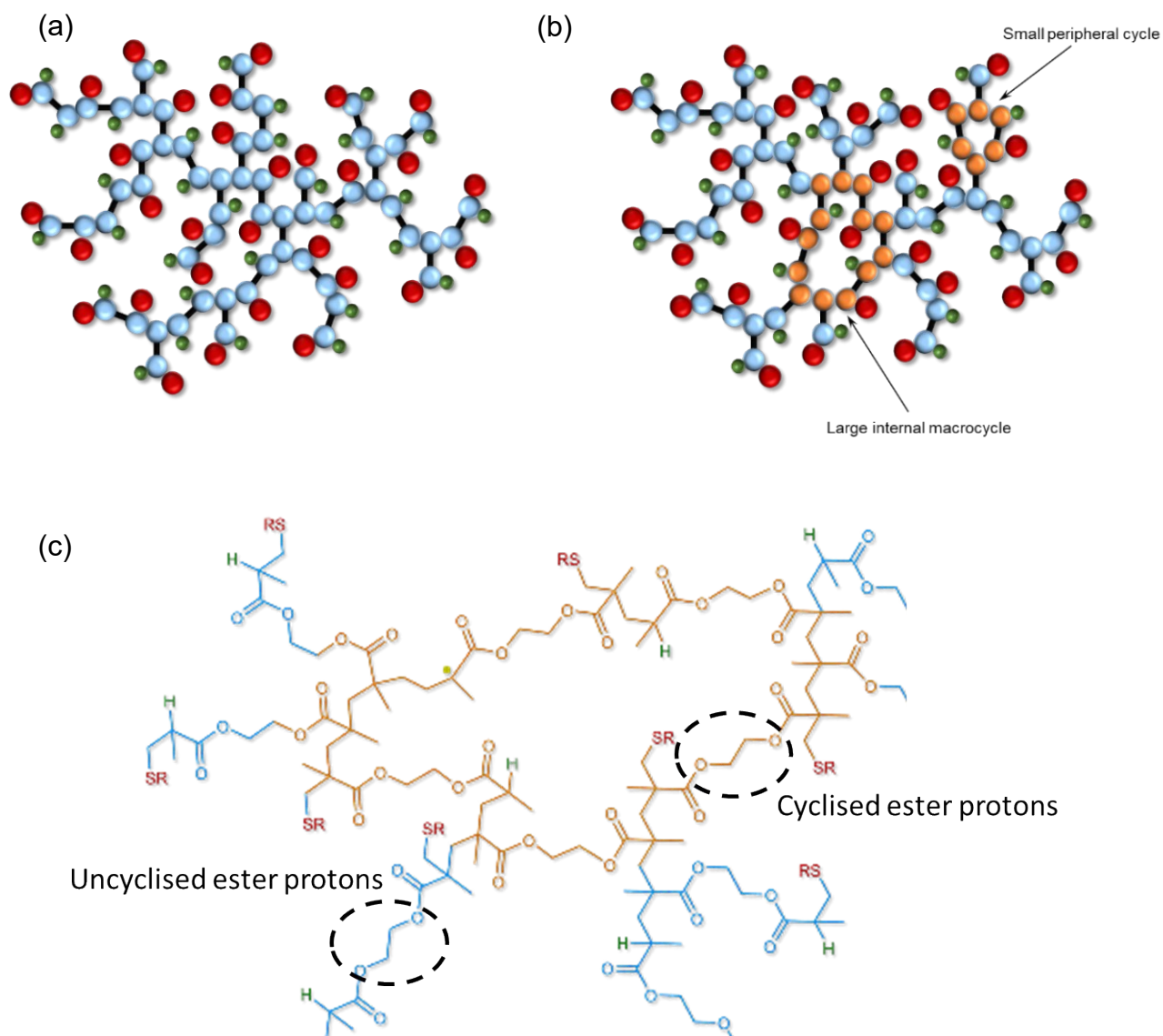


Figure S24 Overlaid inverse-gated ^{13}C NMR spectra (100 MHz, CDCl_3) of the precipitated and dried material [EGDMA]/[DDT] at 50 mg mL^{-1} . Polymerisations conducted at (I) 50 wt%, (II) 60 wt%, (III) 70 wt%, (IV) 80 wt% and (V) 90 wt% solvent highlighting the resonance suppression observed by the in-chain carbons ($\text{C}_{3'}$ and $\text{C}_{4'}$) compared to pendant carbons (C_1 and C_2).



Scheme S2 Schematic representation of (a) 30 divinyl taxogens and 31 telogens in an ideal branched telomerisation polymer architecture, and (b) the formation of macrocyclic substructures within the branched polymer, leading to a decrease in telogen residues relative to divinyl taxogen (31 divinyl taxogens to 30 telogens). (c) Highlighting the difference between cyclised and uncyclized ester protons in the resulting polymer structure.

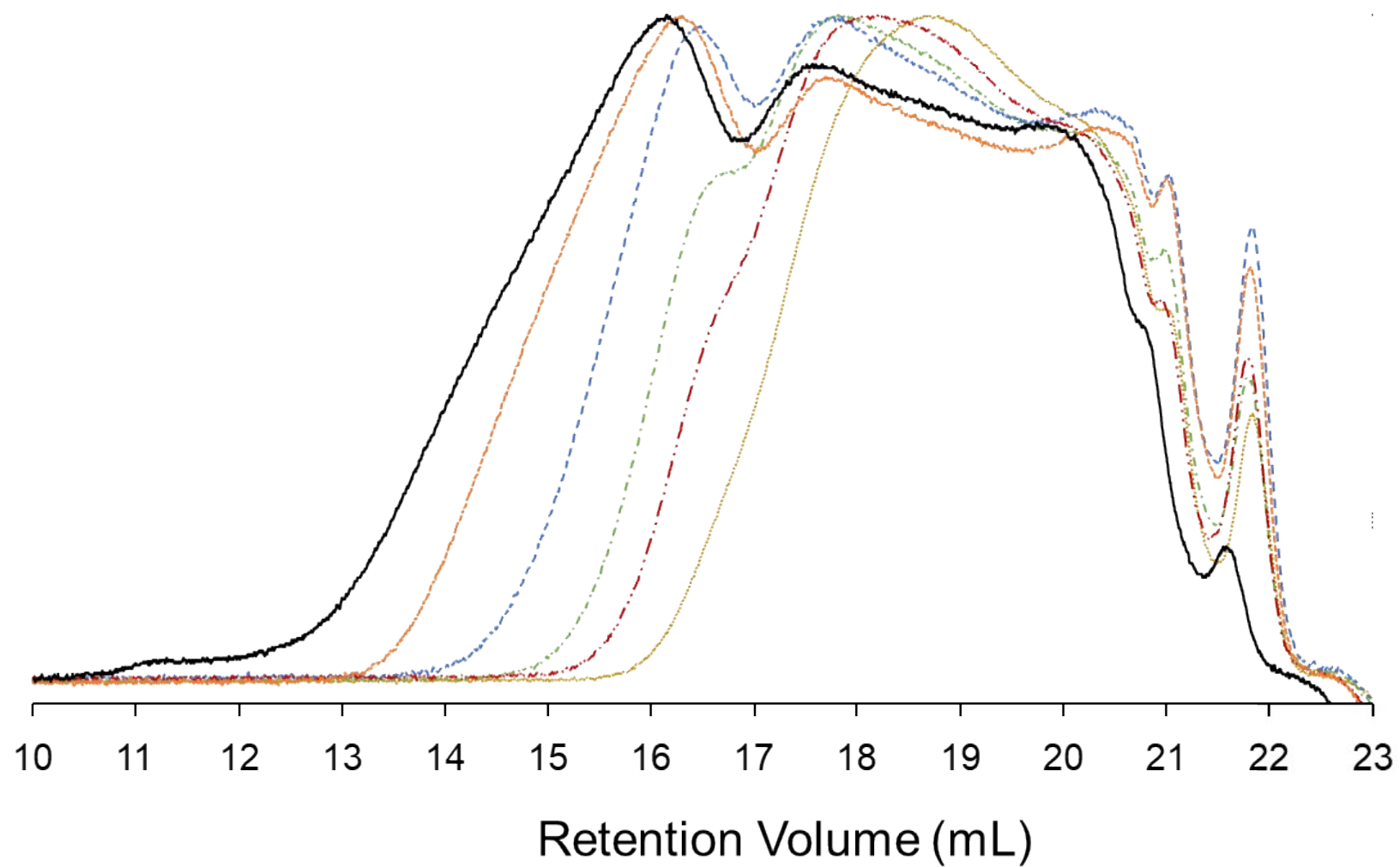


Figure S25 TD-SEC (THF eluent; refractive index (RI) detector signal) showing the molecular weight distributions of branched polymers derived from the $[\text{EGDMA}]_0/[\text{DDT}]_0$ at various EGDMA:DDT ratios conducted at 60 wt% solvent. The overlaid chromatograms show of the distribution of $[\text{EGDMA}]_0/[\text{DDT}]_0 = 0.750$ (yellow round dot line), 0.800 (red dash dot dot line), 0.850 (green dash dot line), 0.900 (blue dash line), 0.950 (orange square dot line) and 1.00 (black solid line) ratios.

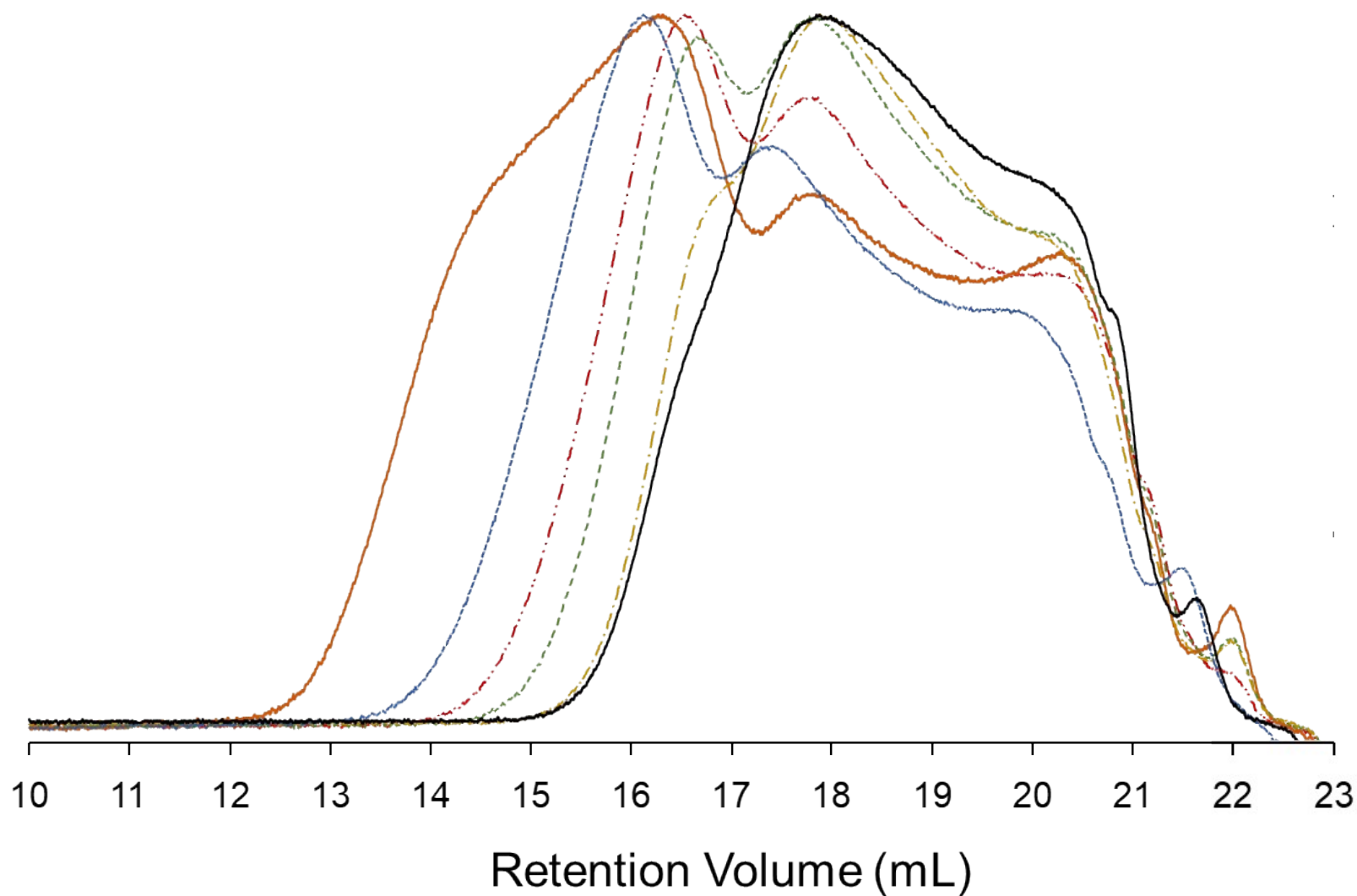


Figure S26 TD-SEC (THF eluent; refractive index (RI) detector signal) showing the molecular weight distributions of branched polymers derived from the $[\text{EGDMA}]_0/[\text{DDT}]_0$ at various EGDMA:DDT ratios conducted at 70 wt% solvent. The overlaid chromatograms show of the distribution of $[\text{EGDMA}]_0/[\text{DDT}]_0 = 1.00$ (black square dot line), 1.05 (red dash dot line), 1.11 (blue dashed line), 1.15 (green dash dot dot line) and 1.18 (orange solid line) ratios.

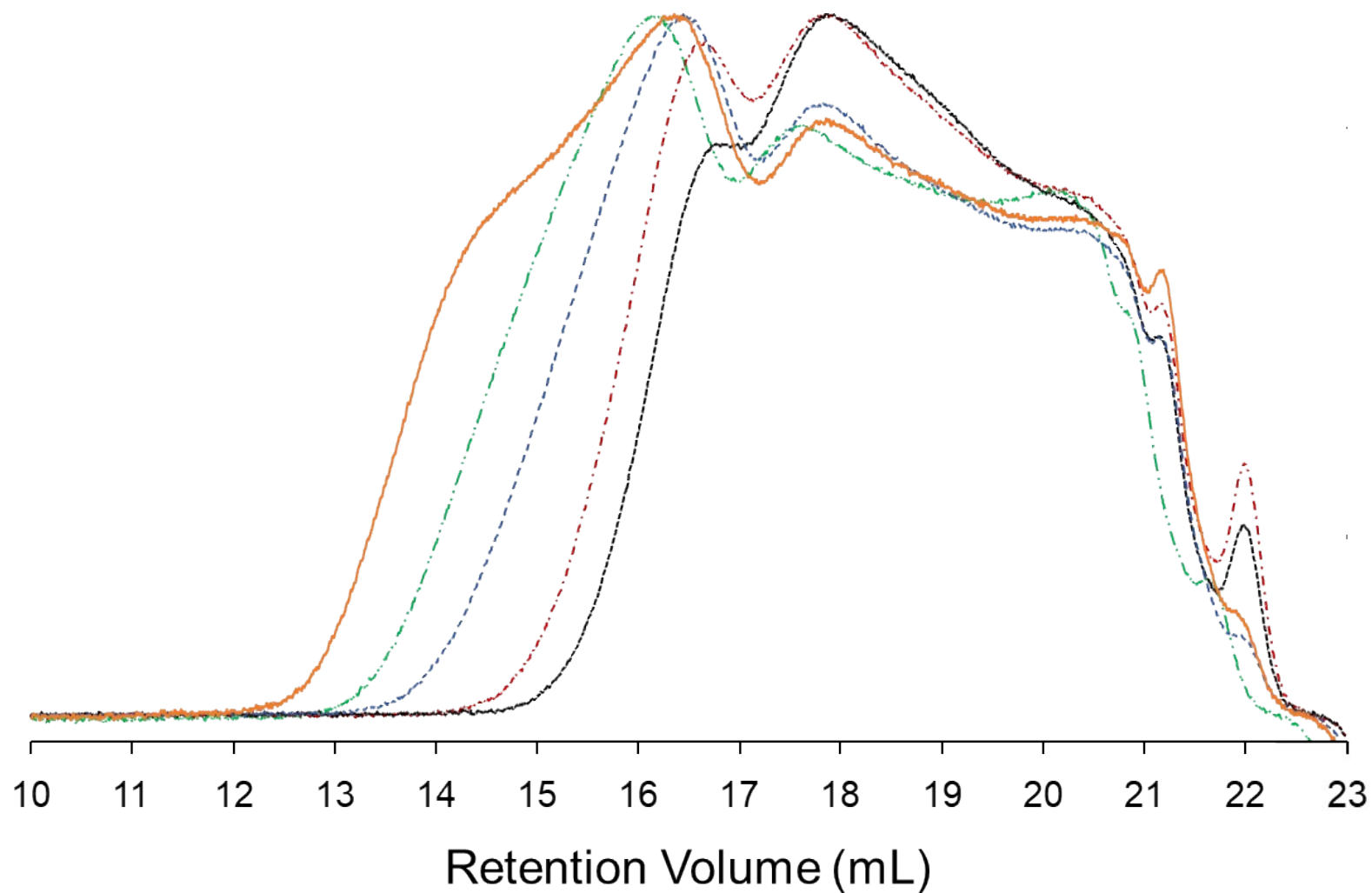


Figure S27 TD-SEC (THF eluent; refractive index (RI) detector signal) showing the molecular weight distributions of branched polymers derived from the $[\text{EGDMA}]_0/[\text{DDT}]_0$ at various EGDMA:DDT ratios conducted at 80 wt% solvent. The overlaid chromatograms show of the distribution of $[\text{EGDMA}]_0/[\text{DDT}]_0 = 1.14$ (black solid line), 1.18 (yellow dash dot line), 1.25 (green dashed line), 1.33 (red dash dot dot line), 1.38 (blue square dot line) and 1.43 (orange solid line) ratios.

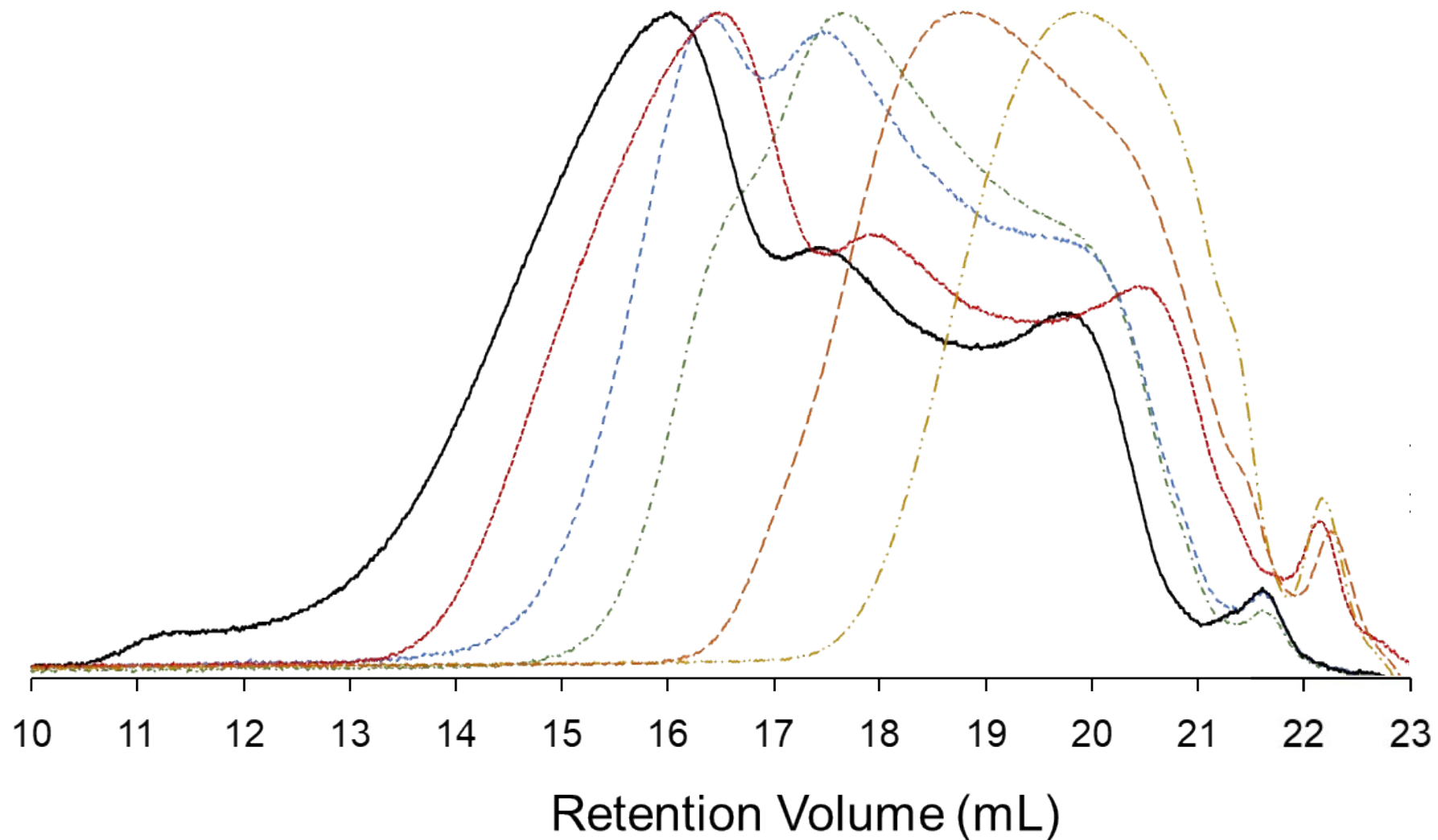


Figure S28 TD-SEC (THF eluent; refractive index (RI) detector signal) showing the molecular weight distributions of branched polymers derived from the $[\text{EGDMA}]_0/[\text{DDT}]_0$ at various EGDMA:DDT ratios conducted at 90 wt% solvent. The overlaid chromatograms show of the distribution of $[\text{EGDMA}]_0/[\text{DDT}]_0 = 1.00$ (yellow dash dot dot line), 1.33 (orange long dash line), 1.55 (green dash dot line), 1.75 (blue short dash line), 2.00 (red square dot line) and 2.10 (black solid line) ratios.

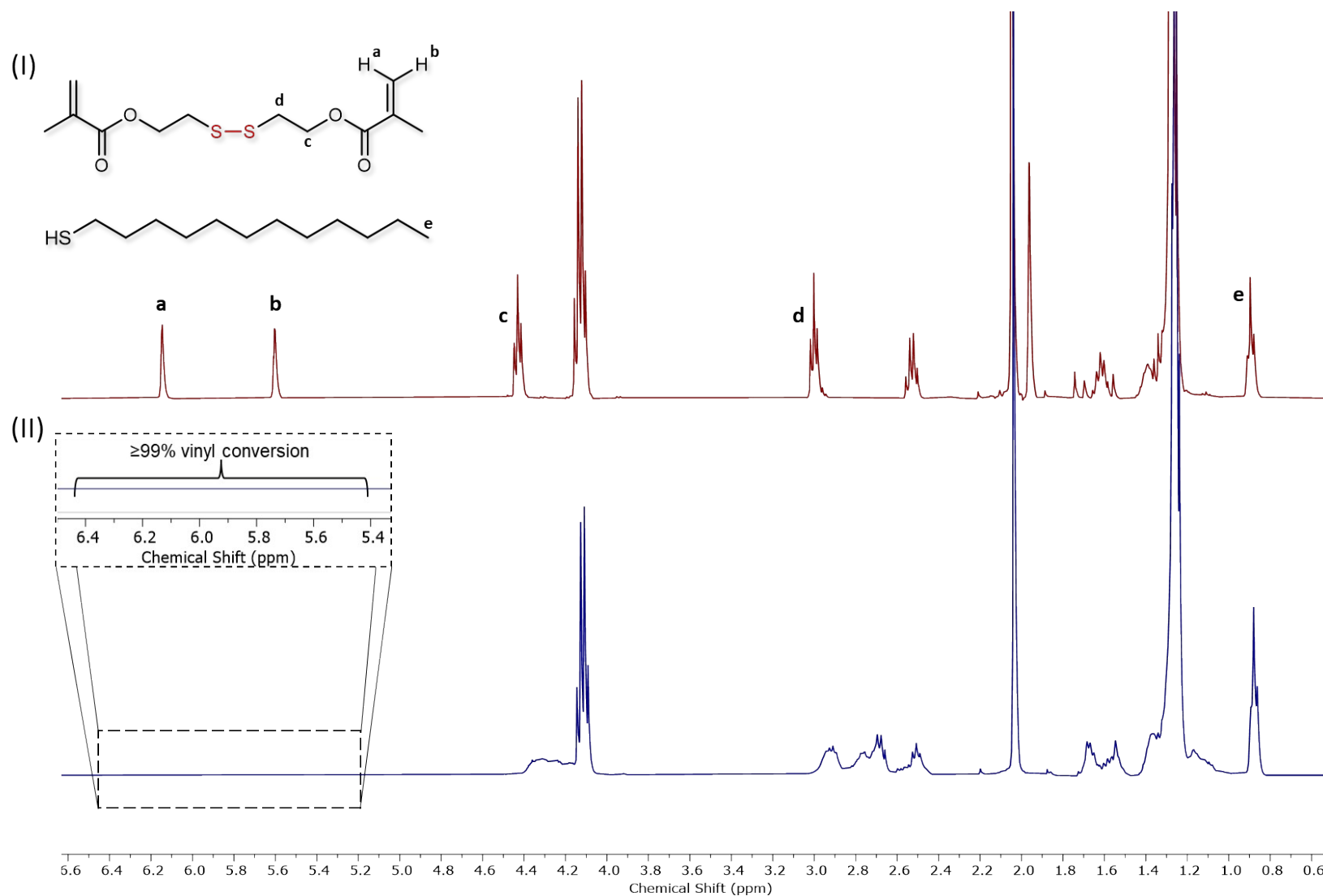


Figure S29 ^1H NMR spectra (400 MHz, CDCl_3) of [DSDMA]/[DDT] in EtOAc. (I) $[\text{DSDMA}]_0/[\text{DDT}]_0 = 0.75$ and (II) the crude sample after 24 hrs showing >99 % vinyl conversion

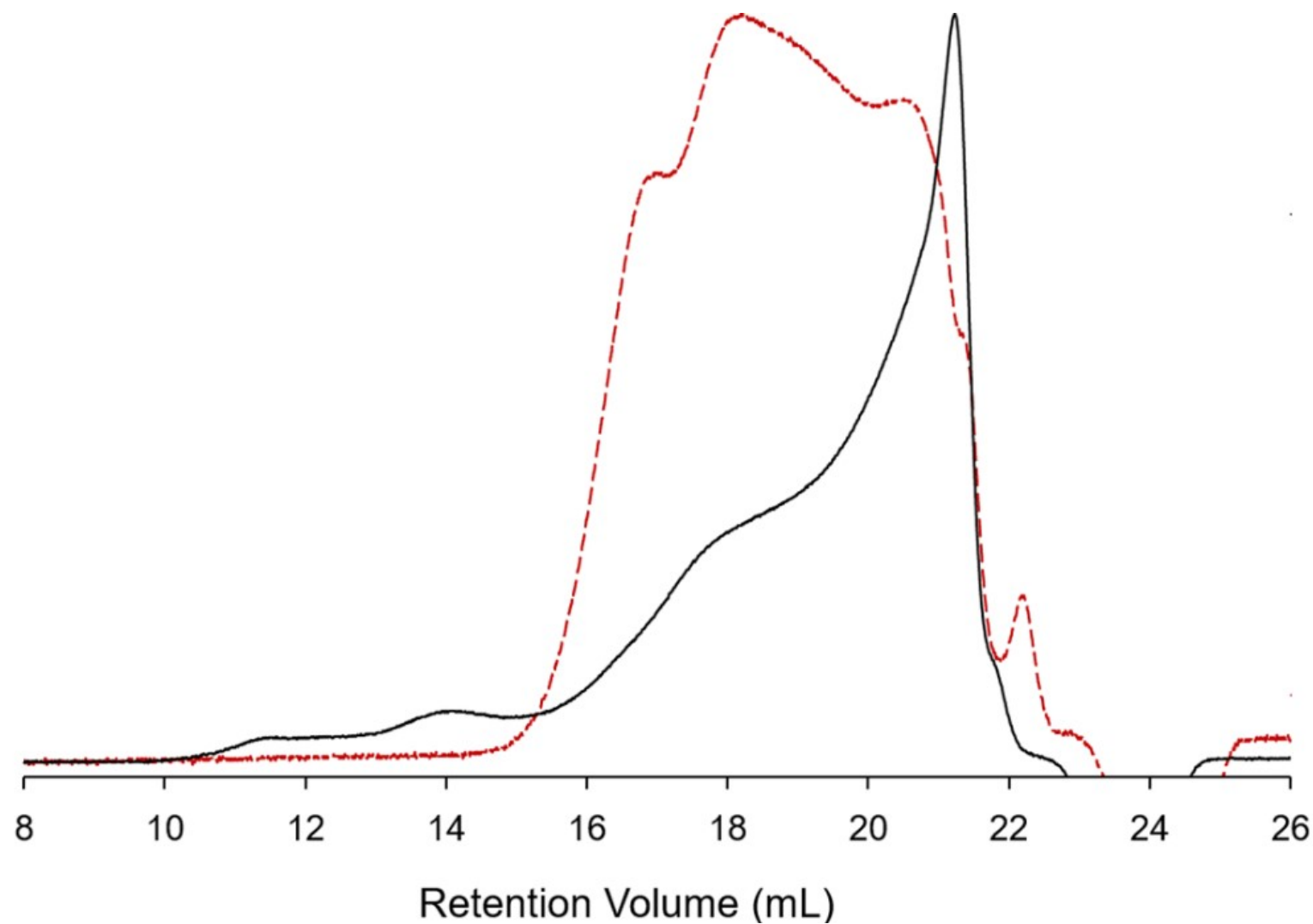


Figure S30 Triple-detection size exclusion chromatography (THF eluent; refractive index (RI) detector signal) showing the normalised molecular weight distribution of branched polymers derived from $[\text{EGDMA}]_0/[\text{DDT}]_0 = 0.75$ (red dashed line) and $[\text{DSDMA}]_0/[\text{DDT}]_0 = 0.75$ (black solid line).

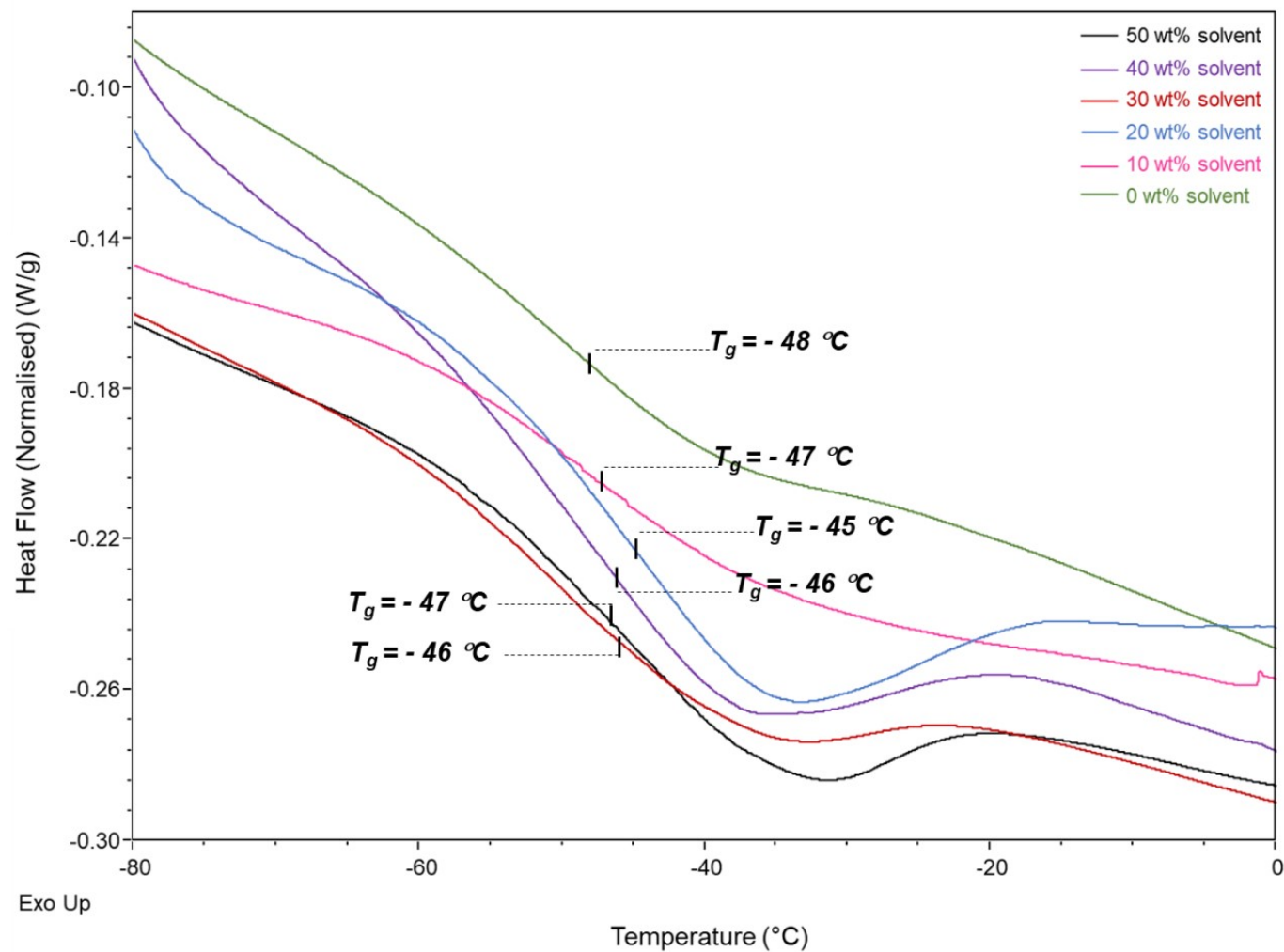


Figure S31 DSC thermographs of purified polymers generated at different reaction concentrations: 50 wt% (black line), 40 wt% solvent (purple line), 30 wt% (red line), 20 wt% (blue line), 10 wt% (pink line) and 0 wt% solvent (green line). DSC analysis was conducted at a heating rate of 10 °C min^{-1} from -90 °C to 150 °C. T_g values across all reaction concentrations observed to be between -45 °C to -48 °C.

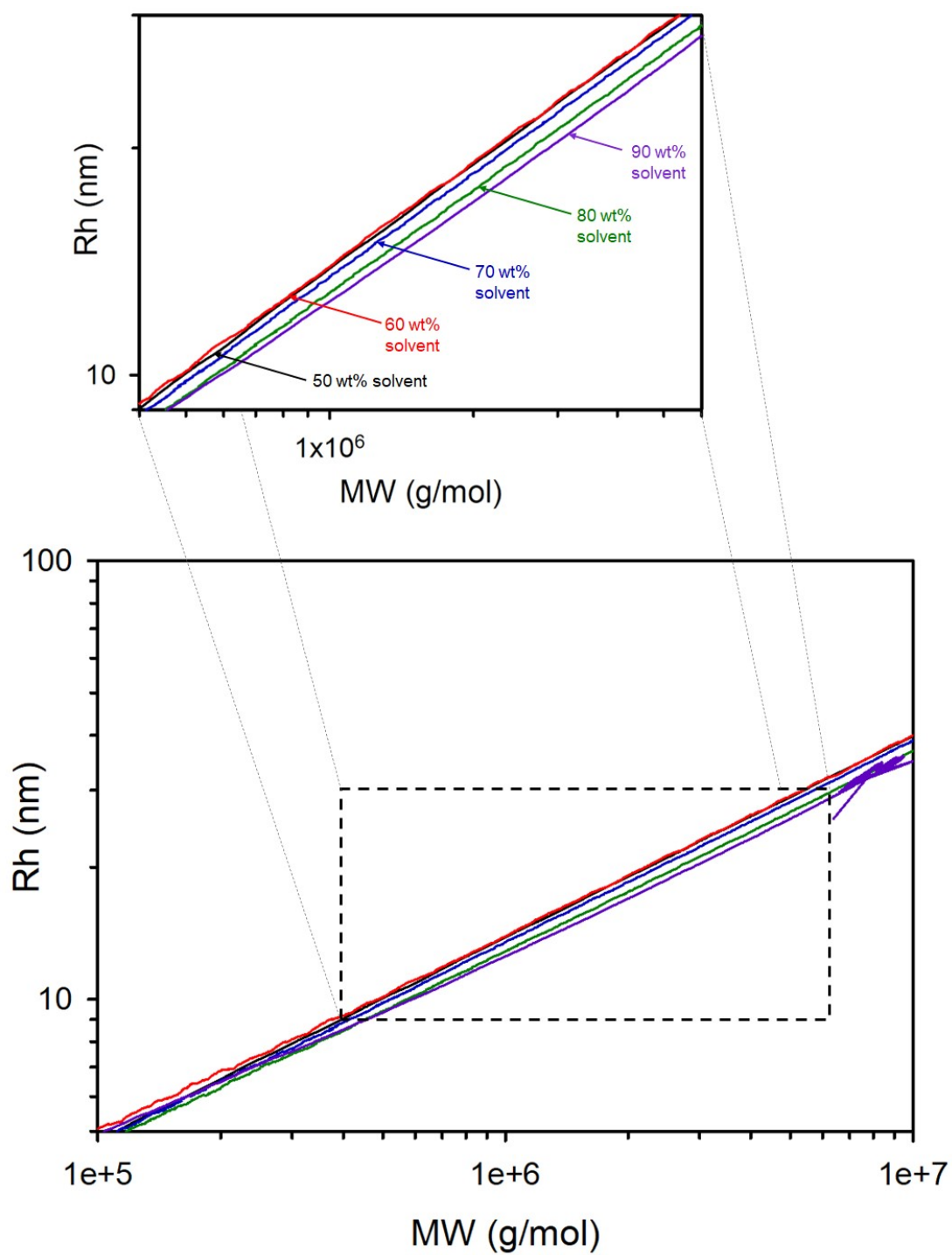


Figure S32 TD-SEC derived analysis of the hydrodynamic radius across the molecular weight distributions for branched polymers generated at 50 wt% solvent (black line), 60 wt% solvent (red line), 70 wt% solvent (blue line), 80 wt% solvent (green line), and 90 wt% solvent (purple line).