

Accessing New and Scalable High Molecular Weight Branched Copolymer Structures using Transfer-dominated Branching Radical Telomerisation (TBRT)

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1. Materials and Instrumentation

1.1 Materials

2,2'-Azobis(2-methylpropionitrile) (AIBN, 98 %), deuterated chloroform (CDCl₃, 99.8 atom % D), deuterated dichloromethane (DCM-d₂, 99.5 atom % D), benzyl methacrylate (BzMA, 96 %), ethylene glycol dimethacrylate (EGDMA, 98 %), methyl methacrylate (MMA, 99 %), bisphenol A dimethacrylate (BPADMA, >98 %), 4-*tert*-butylbenzyl mercaptan (*t*BuBzM), phenyl ethyl mercaptan (PhEM, >99 %), benzyl mercaptan (BzM, 99 %) and cyclohexanethiol (CHT, 97 %) were purchased from Sigma Aldrich. Ethyl Acetate (EtOAc, analytical grade), methanol (MeOH, analytical grade 99.9 %), tetrahydrofuran (THF, HPLC-grade), chloroform (CHCl₃, reagent grade), Toluene (reagent grade) were purchased from Fisher. 1-Dodecanethiol (DDT, 98 %) was purchased from Alfa Aesar. All materials were used as received unless otherwise stated.

1.2 Instrumentation

1.2.1 Nuclear magnetic resonance (NMR) spectroscopy

¹H and ¹³C experiments were recorded using a Bruker AMX-400 MHz spectrometer; ¹H and ¹³C spectra were recorded at a frequency of 400 and 100 MHz respectively. Samples were analysed in CDCl₃ and DCM-d₂ at ambient temperature. ¹H and ¹³C chemical shifts (δ) are reported in parts per million (ppm) relative to those of the internal standard, tetramethyl silane (TMS). ¹³C,¹H Heteronuclear Signal-Quantum Coherence (HSQC), Attached Proton Test (APT), Distortion-Enhanced Polarisation Transfer using a 135° decoupler pulse (DEPT-135) and inverse-gated ¹³C experiments were performed at a (co)polymer concentration of 50 mg mL⁻¹.

1.2.2 Triple-Detection Size-Exclusion Chromatography (TD-SEC)

All TD-SEC analysis of branched (co)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 at 35 °C and a flow-rate of 1 mL min⁻¹. All samples were dissolved at 5 mg mL⁻¹ and passed through a 0.2 μm syringe filter prior to injection (100 μL). From TD-SEC results, the number-average molecular weight (M_n), weight-average molecular weight (M_w), polymer dispersity (Đ), molecular weight distribution and intrinsic viscosity of all (co)polymers were estimated using Omniseq software (version 5.12). Narrow and broad polystyrene standards (Viscotek, M_w = 105 kg mol⁻¹, Đ = 1.050 and M_w = 248 kg mol⁻¹, Đ = 2.370 respectively) were used to ensure correct detector parameters for accurate TD-SEC analysis.

All SEC analysis for linear polymers was performed using a Malvern Viscotek TDA302 instrument using GPCmax autosampler, Viscotek T2000 and T1000 columns in series (and a guard column), a refractive index (RI) detector with a mobile phase of THF at 35 °C and a flow-rate of 1 mL min⁻¹. All samples were dissolved at 10 mg mL⁻¹ with THF as eluent and passed through a 200 nm PTFE syringe filter prior to injection (100 μL). Several poly(methyl methacrylate) standards (Viscotek, M_p = 535 g mol⁻¹, Đ = 1.15; M_p = 1010 g mol⁻¹, Đ = 1.14; M_p = 1760 g mol⁻¹, Đ = 1.15 and M_p = 3040 g mol⁻¹, Đ = 1.08) were used as calibrants to construct a conventional calibration.

Note: The validity of dn/dc determination during TD-SEC in distributions containing very low molecular weight material has been subject to some debate. In conventional CTA-mediated linear polymerisations, one CTA would be incorporated per chain. Variation in dn/dc would be expected for telomer structures as the chain length increases, until a plateau value that is consistent for all higher polymers is achieved. Under TBRT conditions, the thiol is not acting as a chain end but is present in a ratio that is very close to 1:1 – ie the combined MVT+telogen is the actual repeating structure. At low DP, the impact of the thiol is expected to balance more evenly than in conventional linear polymers. No TBRT polymers reported here have extremely low molecular weights as the MVT allows conjoining of telomers into the final high molecular weight polymer. Each polymer has been precipitated to remove all impurities and allow accurate T_g and SEC measurement.

1.2.2 Differential Scanning Calorimetry (DSC)

Thermal analyses were conducted using a TA Instruments Discovery DSC 25 instrument equipped with a RCS90 cooling unit. The following thermal protocol was used for all DSC analyses: (1) the sample was heated to 200 °C and subjected to a 3-minute isotherm to erase its thermal history, (2) the sample was then cooled to -90 °C at a rate of -10 °C min⁻¹ followed by a 30-minute isotherm. (3) glass transition behaviour was then studied during heating of the sample to 150 °C at a rate of 20 °C min⁻¹. Glass transition temperatures (T_g) were recorded using TA Instruments software, TRIOS.

1.2.3 Matrix-Assisted Laser Desorption Ionisation–Time of flight (MALDI-TOF)

Mass spectra of linear species formed under specific telomerisation conditions (telomers and oligomers) were analysed using a Bruker Autoflex Mass Spectrometer (Materials Innovation Factory, Liverpool, UK). Spectra for samples containing MMA were the sum of 5000 shots acquired in positive-reflectron mode. Cesium triiodide (CsI₃) and α -cyano-4-hydroxycinnamic acid (HCCA) were used as the mass scale calibrant and matrix, respectively. Samples were prepared at 10 mg mL⁻¹ in THF. The matrix was dissolved in THF (10 mg mL⁻¹). The solutions were combined at a 5:1 volume ratio of matrix to sample. 2 μL of the obtained solution were deposited onto the stainless-steel sample plate and air dried.

2. Experimental

2.1 Linear polymerisations of MMA

2.1.1 Determination of C_T via Mayo Analysis

In a typical Mayo experiment, MMA (4.00 g, 40.0 mmol, 50 equiv.), DDT (162 mg, 0.800 mmol, 1 equiv.), AIBN (98.4 mg, 0.599 mmol) and EtOAc (4.61 mL, 50 wt%) were added into a round-bottomed flask (10 mL) equipped with a magnetic stirrer bar. A series of 5 reactions were conducted using a $[MMA]_0:[DDT]_0$ feedstock ratios of approximately 1:0 (control reaction), 50:1, 85:1, 100:1, 120:1 and 270:1. The solution was stirred and a sample was extracted for 1H NMR spectroscopic analysis prior to initiation. The solution was purged with N_2 whilst stirring for 15 minutes. The flask sealed and heated to 70 °C under magnetic stirring. The polymerisation was terminated *via* exposure to air and rapid cooling in an ice bath at 15 minutes (< 10% vinyl conversion). This time point is in accordance with the time point pertaining to approximately 5% vinyl conversion as determined during a control FRP kinetic experiment. A sample was then taken from the crude reaction for estimation of monomer conversion by 1H NMR spectroscopy. The crude samples were concentrated and precipitated into cold methanol. The samples were dried in vacuo using a spiral evaporator. The purified samples were then analysed *via* TD-SEC (Table S1, Figure S1). Chain transfer constant measurements for all telogens were conducted in accordance with the procedure outlined above, only varying the telogen used. The telogens studied included: tert-butyl benzyl mercaptan (*t*BuBzM); benzyl mercaptan (BzM); phenyl ethyl mercaptan (PhM) and cyclohexanethiol (CHT).

Table S1 Determination of chain transfer coefficients for various thiol-based CTAs *via* the Mayo method.¹ Polymerisations of MMA conducted at 70 °C in EtOAc at various $[CTA]/[MMA]$ ratios (Initiator: 1.5 mole% based on vinyl bonds).

CTA	Entry	1H NMR ($CDCl_3$)			TD-SEC (THF/TEA)		
		Conv. (%) ^a	$[MMA]/[CTA]^b$	$[CTA]/[MMA]^b$	M_n (g mol ⁻¹) ^c	DP_n^d	$1/DP_n$
DDT	1	4.8	-	0.000000	42 190	421	0.002375
	2	4.8	275	0.003636	24 030	240	0.004167
	3	9.6	116	0.008621	16 365	162	0.006173
	4	8.3	101	0.009901	14 215	142	0.007042
	5	7.4	87	0.011494	12 630	126	0.007937
	6	8.3	50	0.020000	8 915	89	0.011236
<i>t</i> BuBzM	7	4.8	-	0.000000	42 190	421	0.002375
	8	5.0	293	0.003413	26 940	280	0.003571
	9	6.5	133	0.007519	18 030	180	0.005556
	10	7.0	95	0.010526	15 620	156	0.006410
	11	8.5	88	0.011364	14 550	145	0.006897
	12	7.9	50	0.020000	9 325	93	0.010753
BzM	13	4.8	-	0.000000	42 190	421	0.002375
	14	7.1	259	0.003861	26 940	269	0.003717

	15	6.3	124	0.008065	19 015	190	0.005263
	16	4.8	106	0.009434	17 450	174	0.005747
	17	6.0	87	0.011494	15 585	156	0.006410
	18	7.7	49	0.020408	10 510	105	0.009524
PhEM	19	4.8	-	0.000000	42 190	421	0.002375
	20	4.2	225	0.004444	32 070	320	0.003125
	21	6.5	110	0.009091	22 290	223	0.004484
	22	8.5	83	0.012048	20 570	205	0.004878
	23	6.0	47	0.021277	13 925	139	0.007194
CHT	24	4.8	-	0.000000	42 190	421	0.002375
	25	7.7	273	0.003660	39 510	391	0.002558
	26	7.1	127	0.007850	30 020	300	0.003333
	27	5.1	96	0.010400	24 735	247	0.004049
	28	6.8	69	0.014500	23 960	239	0.004184
	29	10.0	47	0.021200	16 130	161	0.006211

^a Determined *via* ¹H NMR spectroscopy of the polymerisation mixture after 15 minutes. ^b Determined *via* ¹H NMR spectroscopy of the polymerisation mixture prior to initiation. ^c Determined by TD-SEC of purified polymers using a THF/TEA mobile phase. ^d Calculated as: $DP_n = (M_n \div M_{r(MMA)})$.

$$\frac{1}{DP_n} = \frac{1}{DP_{n0}} + C_T \frac{[CTA]}{[MMA]}$$

Equation S1

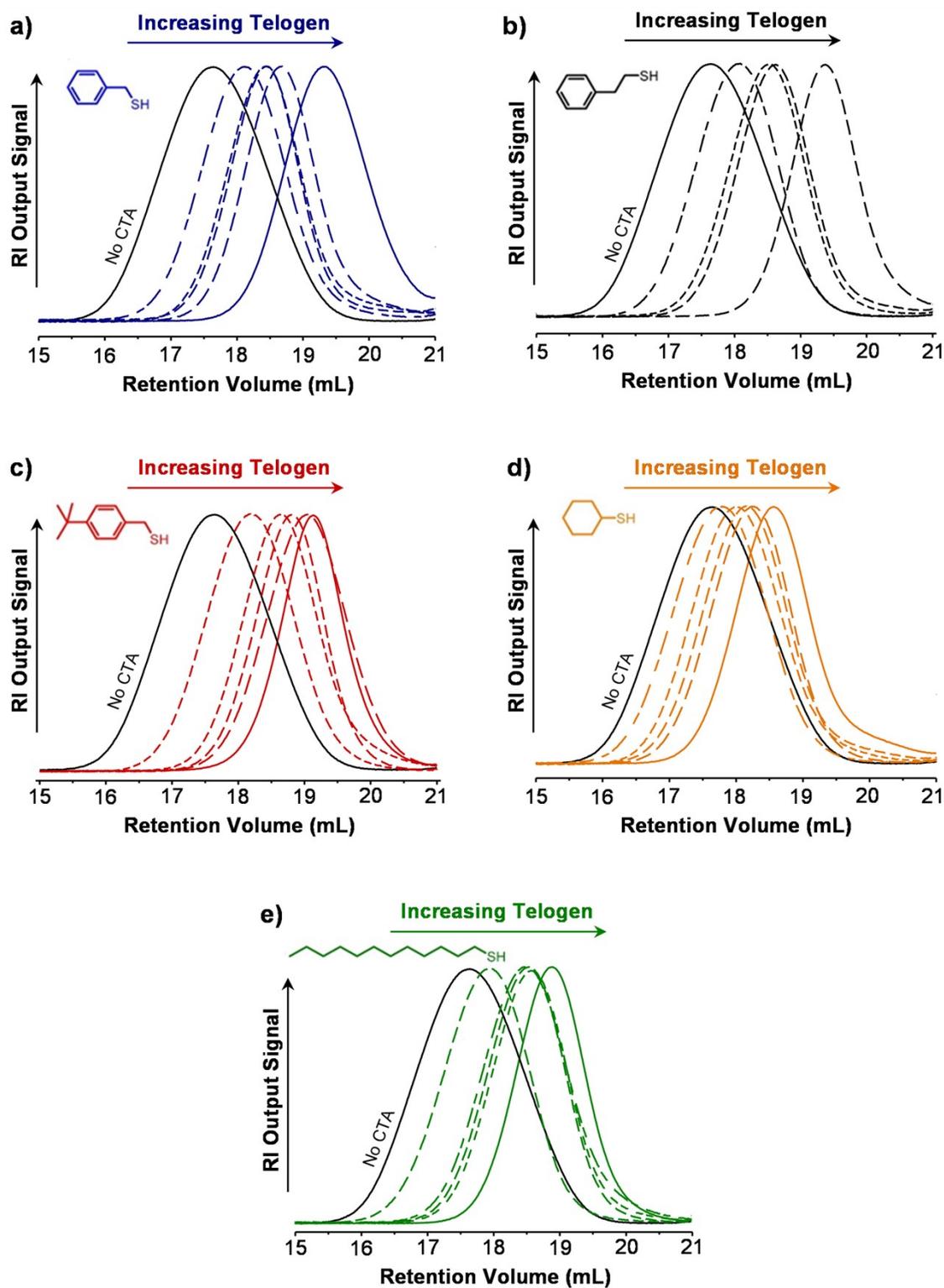


Figure S1 Impact of the initial $[S]/[M]$ ratio on the molecular weight distribution of *poly*(MMA). Overlaid RI chromatograms for *poly*(MMA) obtained at varied initial $[S]/[M]$ ratios using a) BzM, b) PhEM, c) tBuBzM, d) CHT and e) DDT.

2.1.2 Telomerisation of MMA with DDT

MMA (3.00 g, 30.0 mmol, 1.6 equiv.), DDT (3.81 g, 18.8 mmol, 1 equiv.) and AIBN (73.4 mg, 0.450 mmol) were added into a round bottom flask (25 mL) equipped with a magnetic stirrer bar. EtOAc was

added (7.55 mL, 50 wt%) and the resulting solution was purged with N₂ for 15 minutes. At this point a sample was withdrawn (*ca.* 100 μL) and diluted in CDCl₃ allowing for quantification of [MMA]₀/[DDT]₀ by ¹H NMR. The reaction was sealed and left to stir at 70 °C for 24 hours. The reaction was terminated by exposure to air and cooled, at this point a sample (*ca.* 200 μL) was taken for quantification of monomer conversion by ¹H NMR. Integrals of the vinyl protons (5.50 ppm and 6.05 ppm) were compared with integration of the vinyl protons corresponding to the t₀ NMR to determine monomer conversion. The solution was concentrated, and a sample of the crude product was characterised *via* MALDI-TOF (Figure S2) and SEC (Figure S4) with THF eluent.

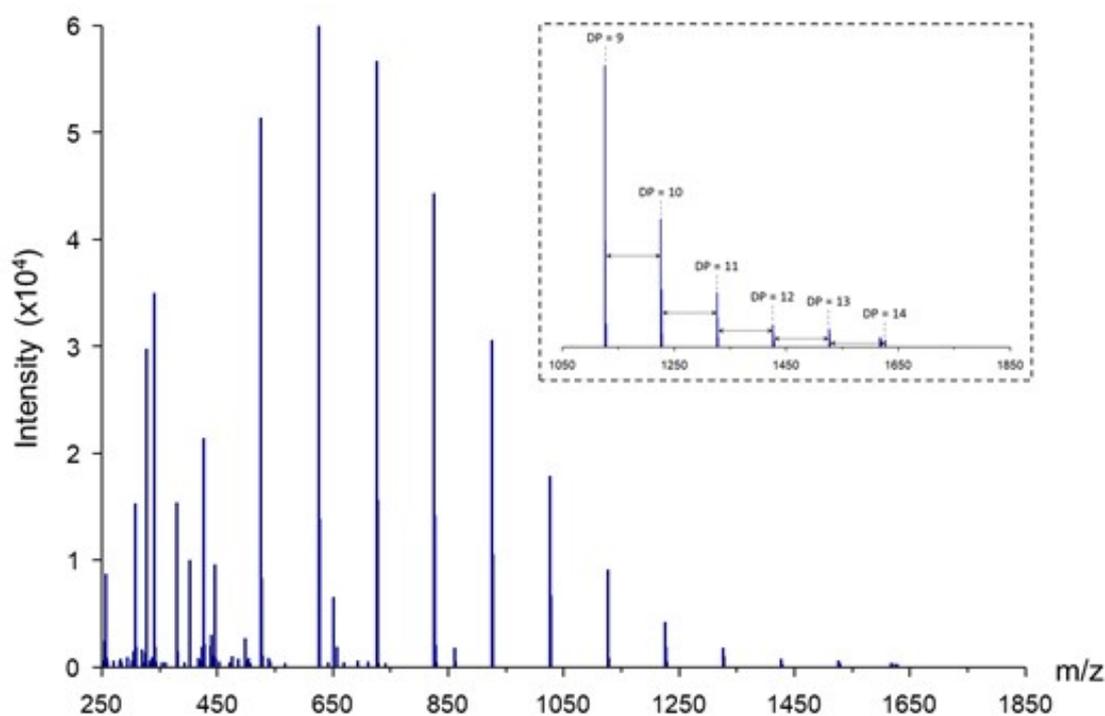


Figure S2 MALDI-TOF mass spectrometry analysis of the crude reaction medium of model MMA telomerisation reaction, [MMA]₀/[DDT]₀ = 1.60 at 50 wt% EtOAc.

2.1.3 Telomerisation of MMA with *t*BuBzM

MMA (3.00 g, 30.0 mmol, 1.6 equiv.), *t*BuBzM (3.39 g, 18.8 mmol, 1 equiv.) and AIBN (73.4 mg, 0.450 mmol) were added into a round bottom flask (25 mL) equipped with a magnetic stirrer bar. EtOAc was added (7.08 mL, 50 wt%) and the resulting solution was purged with N₂ for 15 minutes. At this point a sample was withdrawn (*ca.* 100 μL) and diluted in CDCl₃ allowing for quantification of [MMA]₀/[*t*BuBzM]₀ by ¹H NMR. The reaction was sealed and left to stir at 70 °C for 24 hours. The reaction was terminated by exposure to air and cooled, at this point a sample (*ca.* 200 μL) was taken for quantification of monomer conversion by ¹H NMR. Integrals of the vinyl protons (5.50 ppm and 6.05 ppm) were compared with integration of the vinyl protons corresponding to the t₀ NMR to determine monomer conversion. The solution was concentrated, and a sample of the crude product was characterised *via* MALDI-TOF (Figure S3) and SEC (Figure S4).

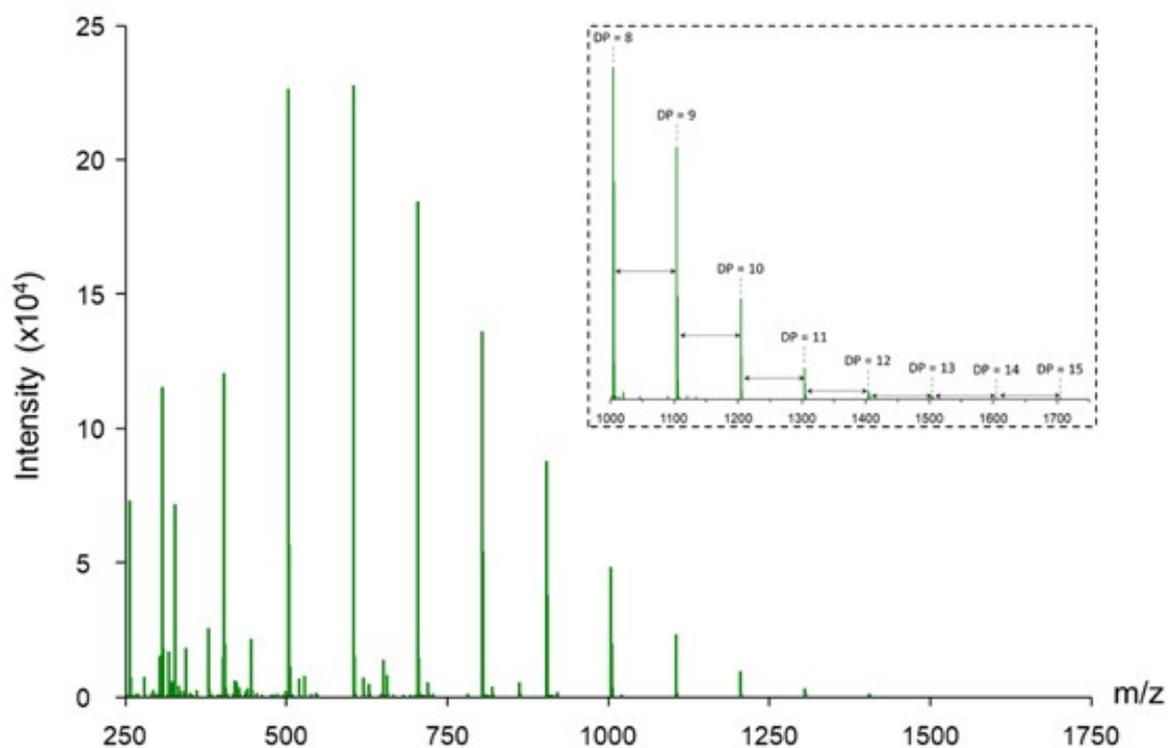


Figure S3 MALDI-TOF mass spectrometry analysis of the crude reaction medium of model MMA telomerisation reaction, $[MMA]_0/[tBuBzM]_0 = 1.60$ at 50 wt% EtOAc.

Table S2 Detailed analysis of the telomerisation of MMA with DDT and *t*BuBzM at 70 °C in EtOAc at 50 wt% (Initiator: 1.5 mole% AIBN based on vinyl bonds).

^a Determined by ¹H NMR of reaction medium prior to initiation. ^b Determined by ¹H NMR of crude reaction mixture after 24 hrs. ^c Determined by SEC in THF.

Telogen	¹ H NMR (CDCl ₃)		SEC (THF) ^c			
	$\frac{[MMA]_0}{[Telogen]_0}$ ^a	Vinyl Conv. (%) ^b	M_w (g mol ⁻¹)	M_n (g mol ⁻¹)	M_p (g mol ⁻¹)	\bar{D}
DDT	1.60	> 99	686	619	483	1.11
<i>t</i> BuBzM	1.60	> 99	574	547	523	1.05

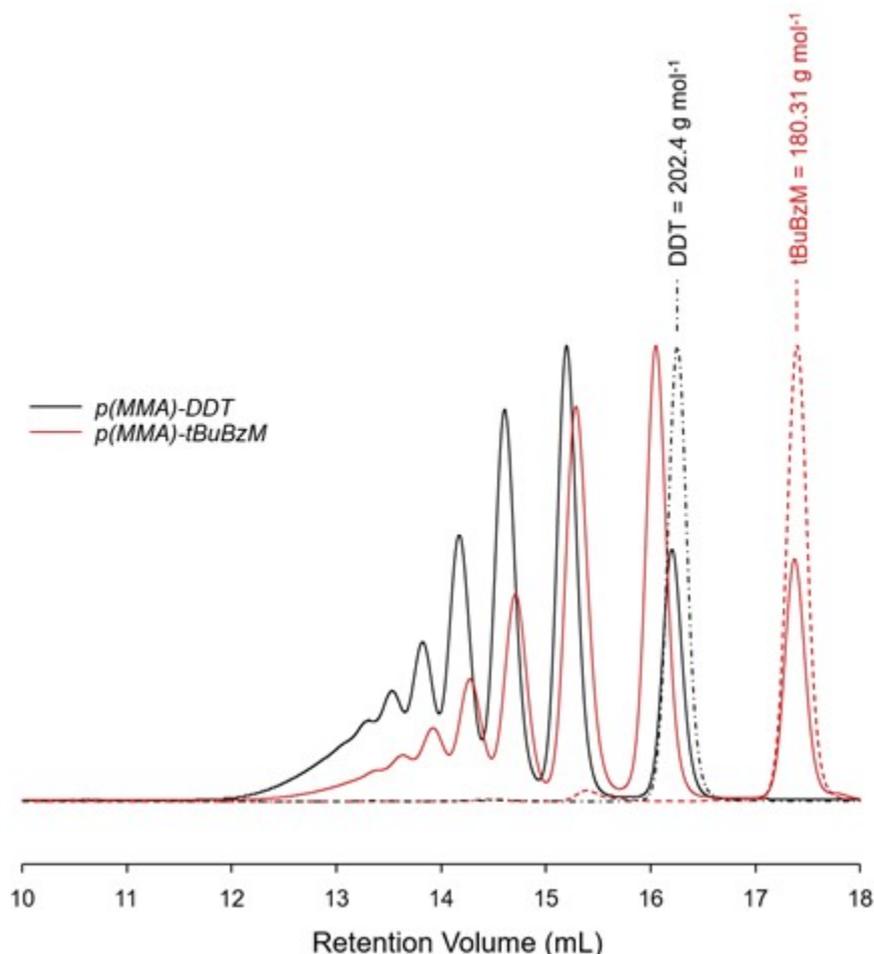


Figure S4 SEC (THF; refractive index (RI) detector signal) showing the molecular weight distribution of linear telomers derived from MMA with DDT (black solid line) and MMA with *t*BuBzM (red solid line), both at an initial taxogen:telogen ratio of 1.60:1. The overlaid chromatograms show of the distribution of telomers conducted at 50 wt% in EtOAc and pure telogens (DDT, black dash dot line and *t*BuBzM, red dashed line).

2.1.4 Determination of C_T during linear telomerisations of MMA

Measurement of chain transfer constant of DDT and *t*BuBzM under telomerisation conditions was conducted in accordance with the procedure outlined above, on a 4.00 g scale.

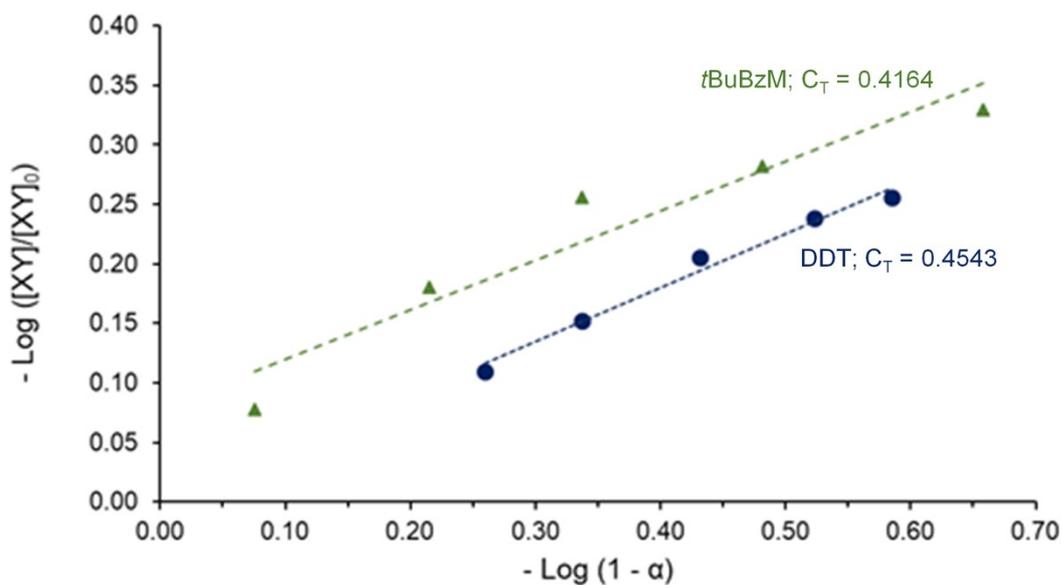
In the kinetic experiment of $[MMA]_0/[DDT]_0 = 1.60$, samples (ca. 500 μ L) were taken at pre-determined time points from the reaction medium under positive N_2 pressure and stopped *via* simultaneous exposure to oxygen and cooling the reaction solution in an ice bath. Quantification of monomer and thiol conversion was determined by 1H NMR and inverse-gated ^{13}C NMR spectroscopy, respectively in $CDCl_3$ using crude samples of the reaction medium. Integrals of the vinyl protons (5.50 ppm and 6.05 ppm) were compared with integration of the vinyl protons corresponding to the t_0 NMR to determine monomer conversion. Integrals of the methylene carbons adjacent to thiol (24.6 ppm) were compared with integration of the methylene group adjacent to the ethyl end-group (31.9 ppm) corresponding to all thiododecyl fragments to determine thiol conversion.

Chain transfer constant measurements of *t*BuBzM were conducted in accordance with the procedure outlined above. Thiol conversion was determined using integrals of the methylene carbon adjacent to thiol (28.0 ppm) and compared to the integration of the tertiary methyl group (31.4 ppm) corresponding to all *t*BuBzM fragments to determine thiol conversion.

Table S3 Rates of consumption of vinyl and thiol functionalities in the telomerisation of [MMA]₀/[DDT]₀ = 1.5 and [MMA]₀/[*t*BuBzM]₀ = 1.5 at 70 °C in EtOAc at 50 wt% (Initiator: 1.5 mole% AIBN based on vinyl bonds).

Telogen (XY)	Time (mins)	¹³ C NMR (CDCl ₃) ^a		-Log([XY]/[XY] ₀)	-Log(1 - α)
		[XY] Remaining (%)	Vinyl Conv. (α, %)		
DDT	30	20.7	45	0.1101	0.2596
	60	18.8	54	0.1519	0.3372
	90	16.6	63	0.2059	0.4318
	120	15.4	70	0.2385	0.5229
	150	14.8	74	0.2558	0.5850
<i>t</i> BuBzM	30	22.3	16	0.0777	0.0757
	60	17.6	39	0.0181	0.2147
	90	14.8	54	0.2558	0.3372
	120	13.9	67	0.2824	0.4815
	150	12.5	76	0.3291	0.6198
	180	11.0	83	0.3846	0.7696

^a Determined by inverse-gated ¹³C NMR of crude samples taken at pre-determined intervals, referenced against samples analysed at t₀.



$$\log \frac{[XY]}{[XY]_0} = C_T \log(1 - \alpha)$$

Equation S2

Figure S5 Relative rates of vinyl and thiol consumption during the telomerisation of $[MMA]_0/[DDT]_0 = 1.5$ (blue circles) and $[MMA]_0/[tBuBzM]_0 = 1.5$ (green triangles) at 70 °C in EtOAc at 50 wt%.

2.2 (Co)polymer synthesis *via* transfer-dominated branching radical (co)telomerisation

2.2.1 Synthesis & characterisation of *p*(DDT-EGDMA)

EGDMA (5.00 g, 25.2 mmol, 0.850 equiv.), DDT (6.01 g, 29.7 mmol, 1.00 equiv.) and AIBN (0.124 g, 0.756 mmol) were placed into a 25 mL round-bottom flask. Ethyl acetate (50 wt % based on EGDMA and DDT; 11.01 g, 12.21 mL) was added and the solution was deoxygenated using a nitrogen purge under magnetic stirring for 30 minutes. An aliquot (~100 μ L) of the mixture was taken for determination of the molar ratio of EGDMA to DDT prior to initiation ($[EGDMA]_0/[DDT]_0$) by ^1H NMR (Figure S6). The flask was then placed in an oil bath at 70 °C for 24 hours. The reaction was stopped *via* cooling and exposure to air. An aliquot (~100 μ L) of the reaction mixture was taken for determination of monomer conversion *via* ^1H NMR (Figure S7). The reaction mixture was then diluted in THF and precipitated into methanol (using a good solvent: anti-solvent volume ratio of 1:10) at ambient temperature, yielding a white precipitate. The polymer was dried *in vacuo* at 40 °C overnight to yield *p*(DDT-EGDMA) as a white solid. The product was analysed by TD-SEC (Figure S8) and both ^1H and ^{13}C NMR spectroscopy (Figure S9-S10).

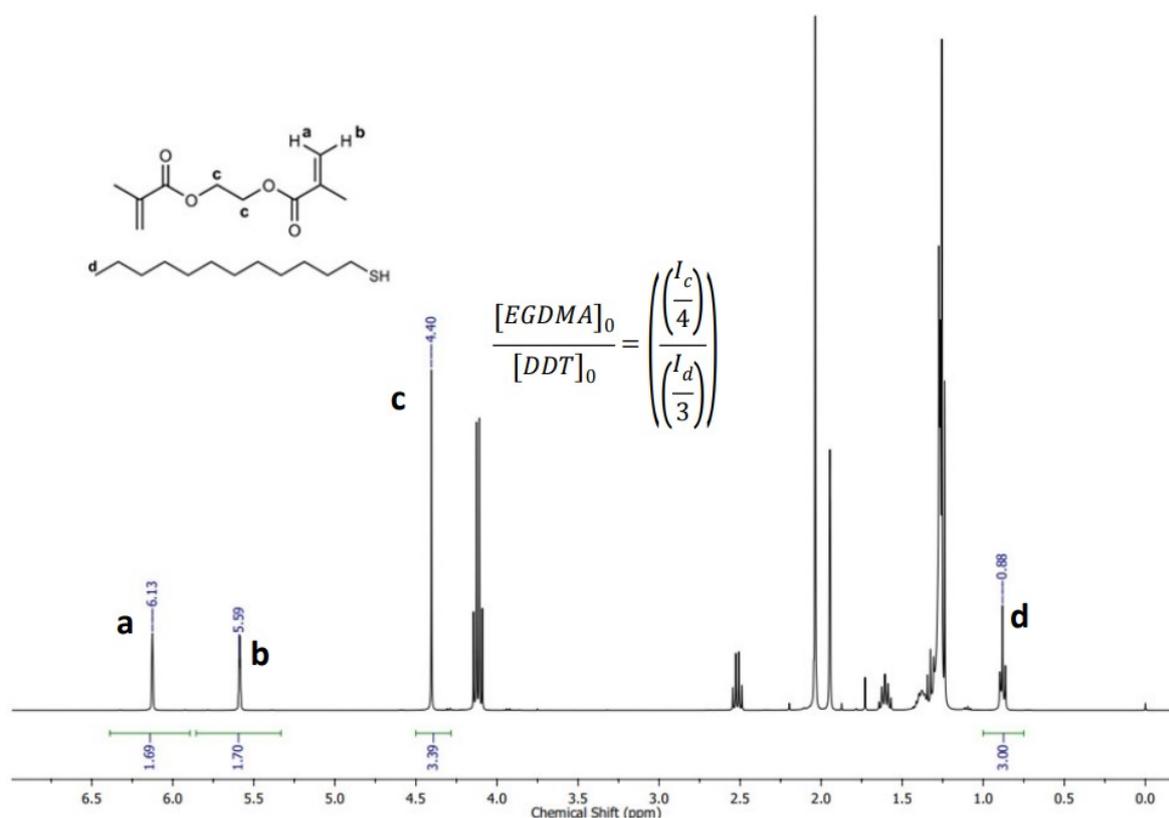


Figure S6 ^1H NMR (400 MHz, CDCl_3) spectrum obtained from the homopolymerisation of EGDMA with DDT prior to thermal initiation ($t = 0$). The equation provided was used to determine the initial ratio of EGDMA to DDT ($[\text{EGDMA}]_0/[\text{DDT}]_0$).

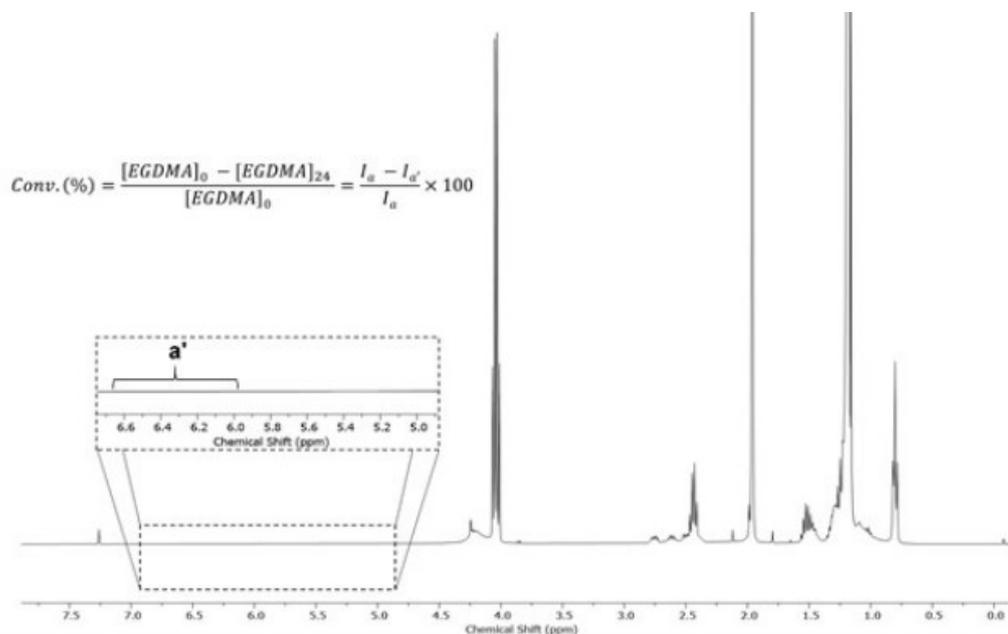


Figure S7 ^1H NMR (400 MHz, CDCl_3) of $[\text{EGDMA}]_0/[\text{DDT}]_0 = 0.85$ at $t = 24$ hours (crude reaction mixture) showing the absence of vinyl peaks. Calculation of the monomer conversion of EGDMA at 24 hours, using the integrals from the chemical shifts at 5.5 ppm and 6.0 ppm at $t = 0$ (H_a) and at $t = 24$ hours ($H_{a'}$), following normalisation of the methyl group on DDT at 0.88 ppm to 3H.

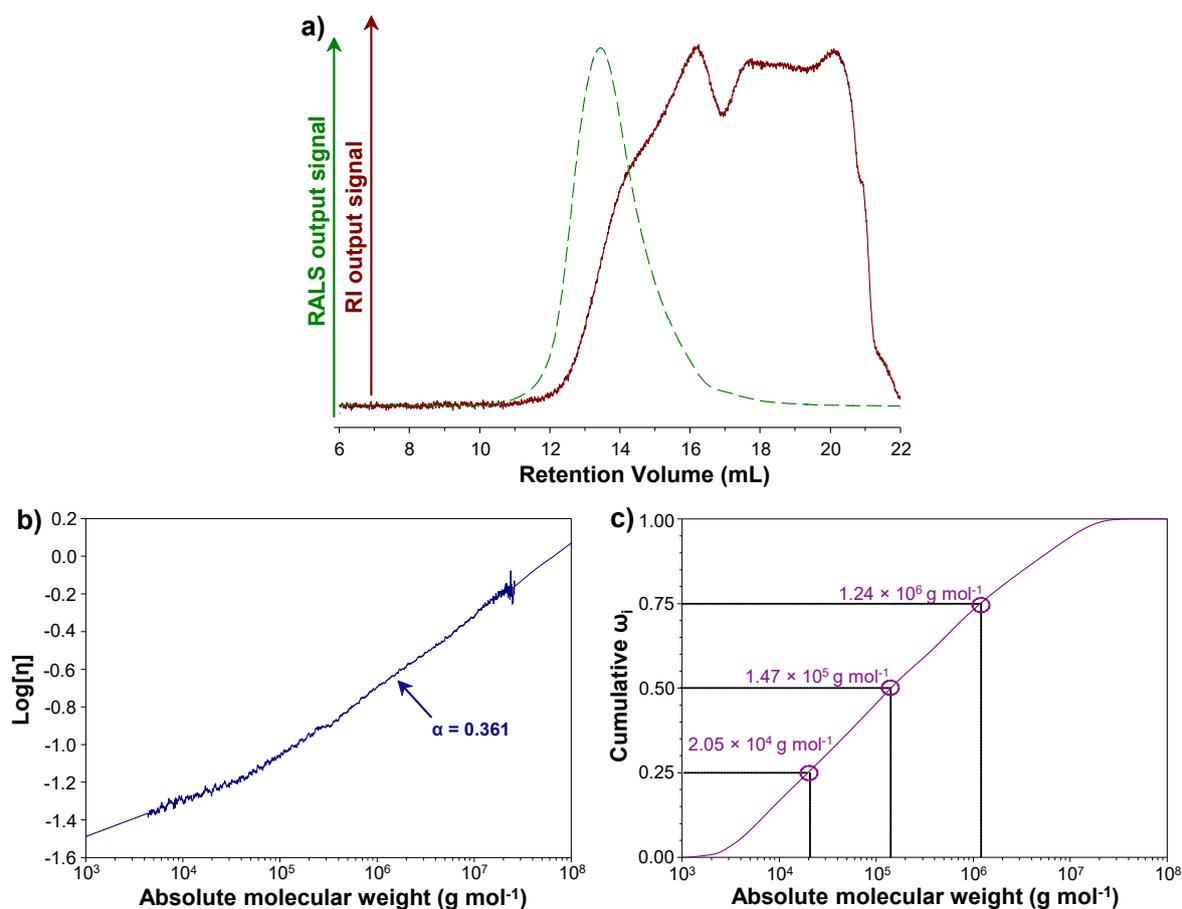


Figure S8 TD-SEC analysis of *p*(DDT-EGDMA). a) Overlaid RI (red solid line) and RALS (green dashed line) chromatograms. b) Evaluation of polymer topological structure *via* MHS analysis. c) Analysis of the relationship between absolute molecular weight and the cumulative weight fraction.

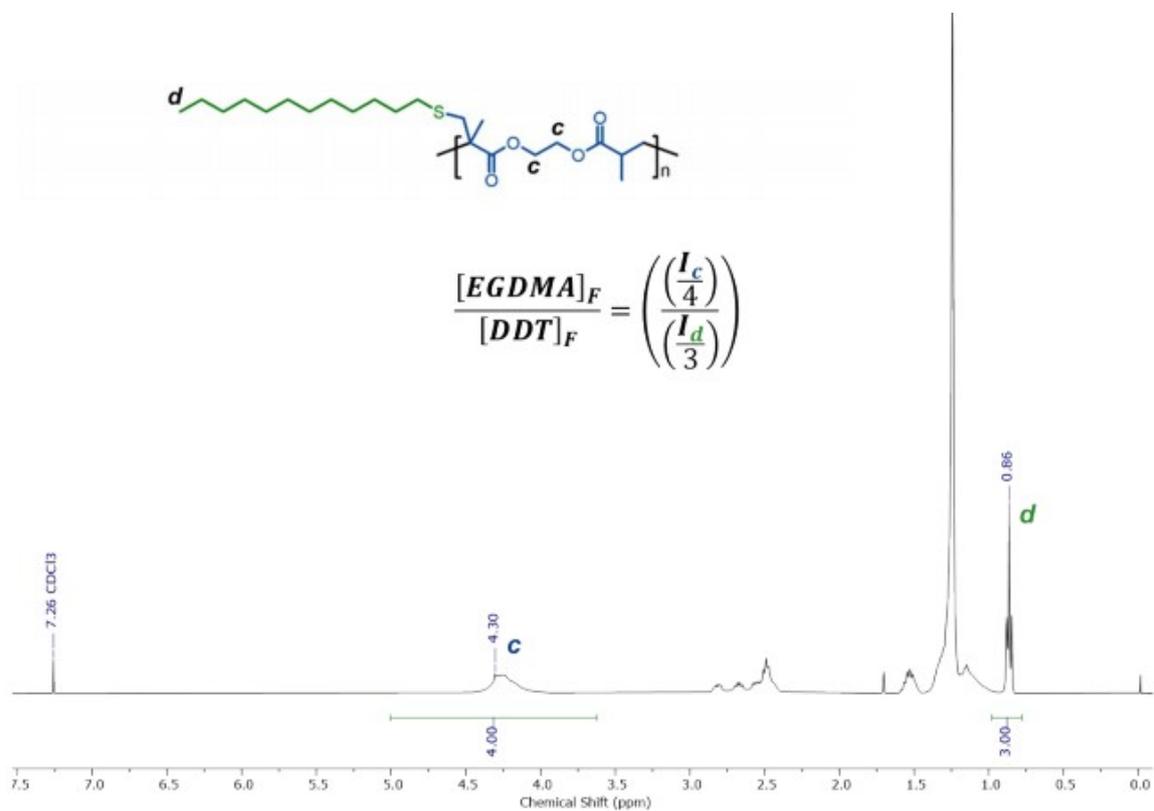


Figure S9 ^1H NMR (400 MHz, CDCl_3) analysis of $p(\text{DDT-EGDMA})$ showing the calculation used to determine the final molar ratio of EGDMA to DDT in the purified polymer ($[\text{EGDMA}]_{\text{F}}/[\text{DDT}]_{\text{F}}$).

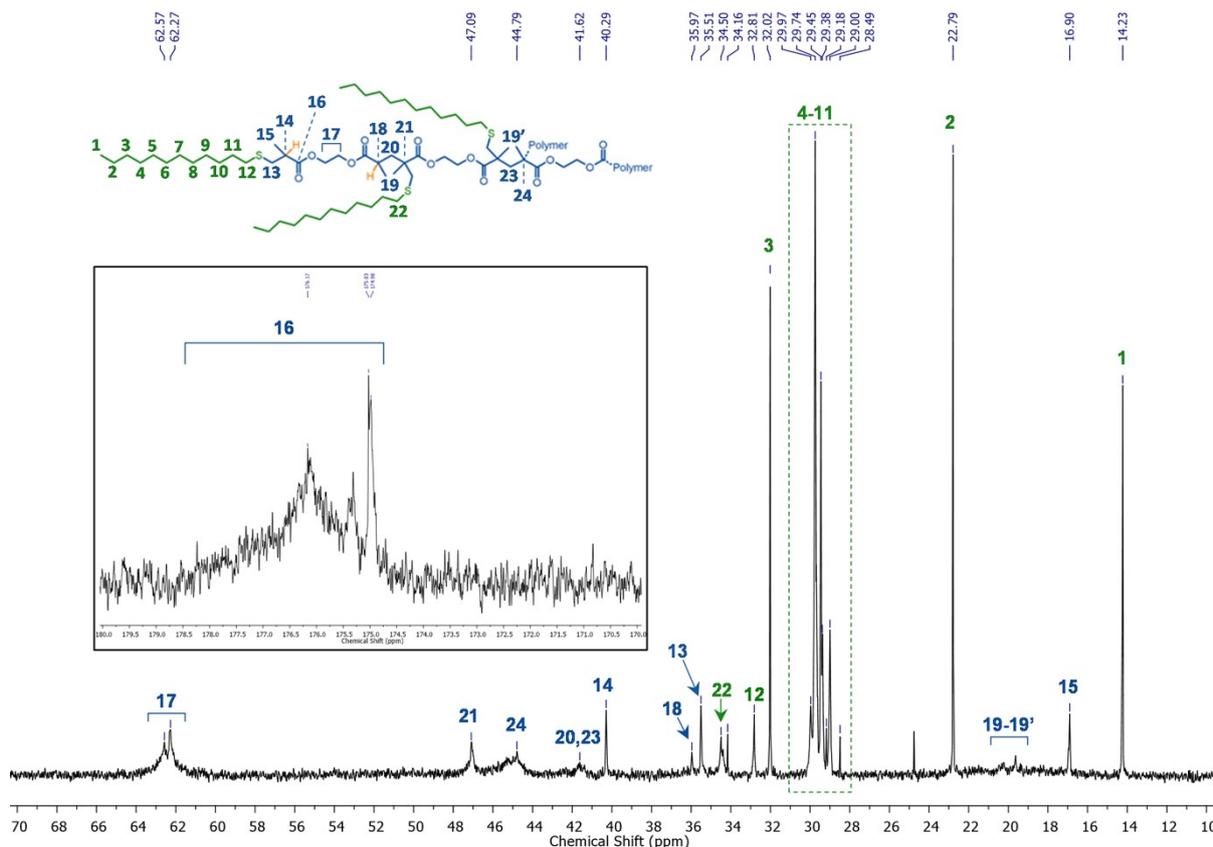


Figure S10 ^{13}C NMR (100 MHz, CDCl_3) spectrum of $p(\text{DDT-EGDMA})$ including assignment of ^{13}C environments.

2.2.2 Synthesis & characterisation of $p(t\text{BuBzM-EGDMA})$

EGDMA (5.00 g, 25.2 mmol, 0.825 equiv.), $t\text{BuBzM}$ (5.51 g, 30.6 mmol, 1.00 equiv.) and AIBN (0.124 g, 0.756 mmol) were placed into a 25 mL round-bottom flask. Ethyl acetate (50 wt % based on EGDMA and DDT; 10.63 g, 11.78 mL) was added and the solution was deoxygenated using a nitrogen purge under magnetic stirring for 30 minutes. An aliquot ($\sim 100 \mu\text{L}$) of the mixture was taken for determination of the molar ratio of EGDMA to $t\text{BuBzM}$ prior to initiation ($[\text{EGDMA}]_0/[\text{tBuBzM}]_0$) by ^1H NMR (Figure S11). The flask was then placed in an oil bath at 70°C for 24 hours. The reaction was stopped *via* cooling and exposure to air. An aliquot ($\sim 100 \mu\text{L}$) of the reaction mixture was taken for determination of monomer conversion *via* ^1H NMR (Figure S12). The reaction mixture was then diluted in THF and precipitated into methanol (using a good solvent: anti-solvent volume ratio of 1:20) at ambient temperature, yielding a white precipitate. The polymer was dried *in vacuo* at 40°C overnight to yield $p(t\text{BuBzM-EGDMA})$ as a white powder. The product was analysed by TD-SEC (Figure S13) and several ^1H and ^{13}C NMR spectroscopic techniques (Figure S14-S17).

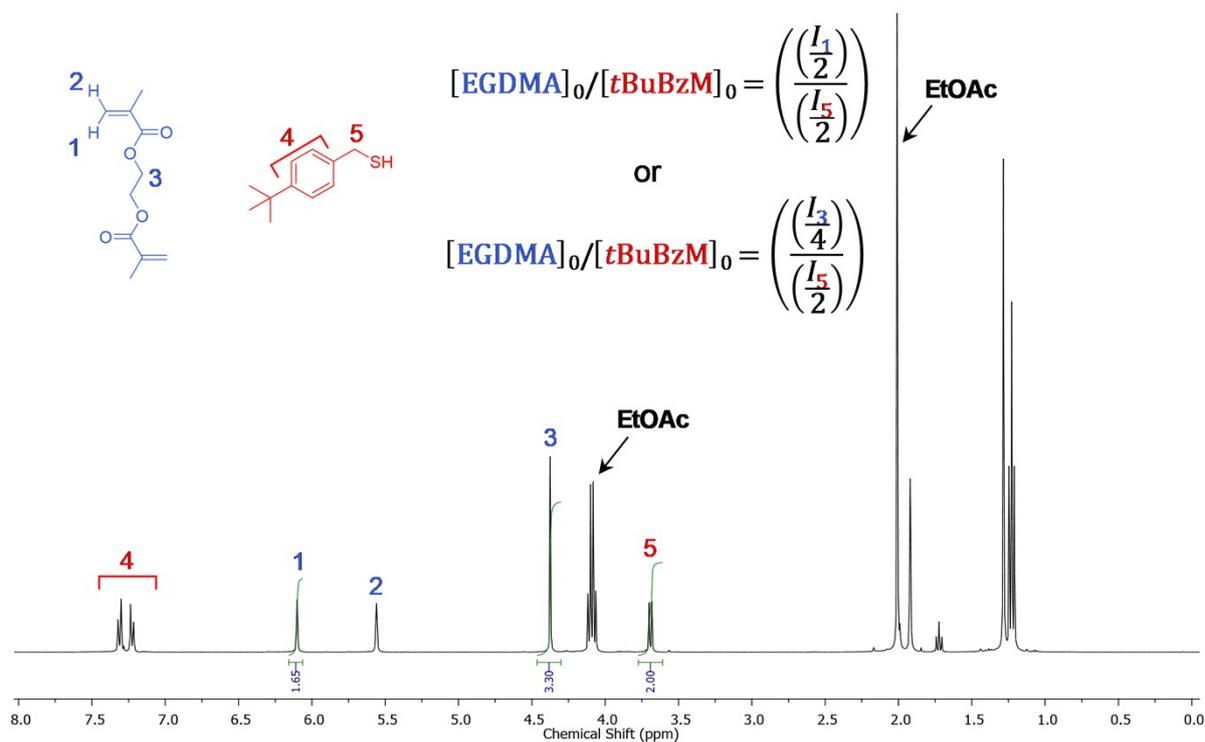


Figure S11 ^1H NMR (400 MHz, CDCl_3) spectrum obtained from the homopolymerisation of EGDMA with *t*BuBzM prior to thermal initiation ($t = 0$). The equations provided were used to determine the initial ratio of EGDMA to *t*BuBzM ($[\text{EGDMA}]_0/[\text{tBuBzM}]_0$).

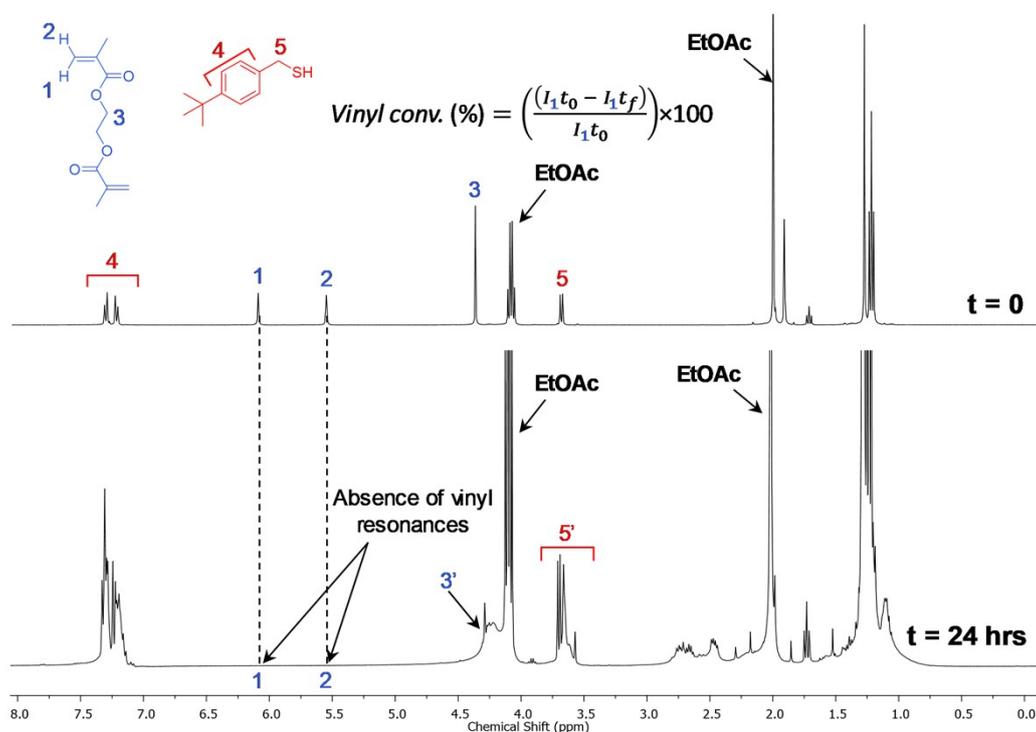


Figure S12 Overlaid ^1H NMR (400 MHz, CDCl_3) spectra obtained from the homopolymerisation of EGDMA with *t*BuBzM prior to thermal initiation (top) and 24 hours after initiation (bottom). The equation provided was used to determine monomer conversion.

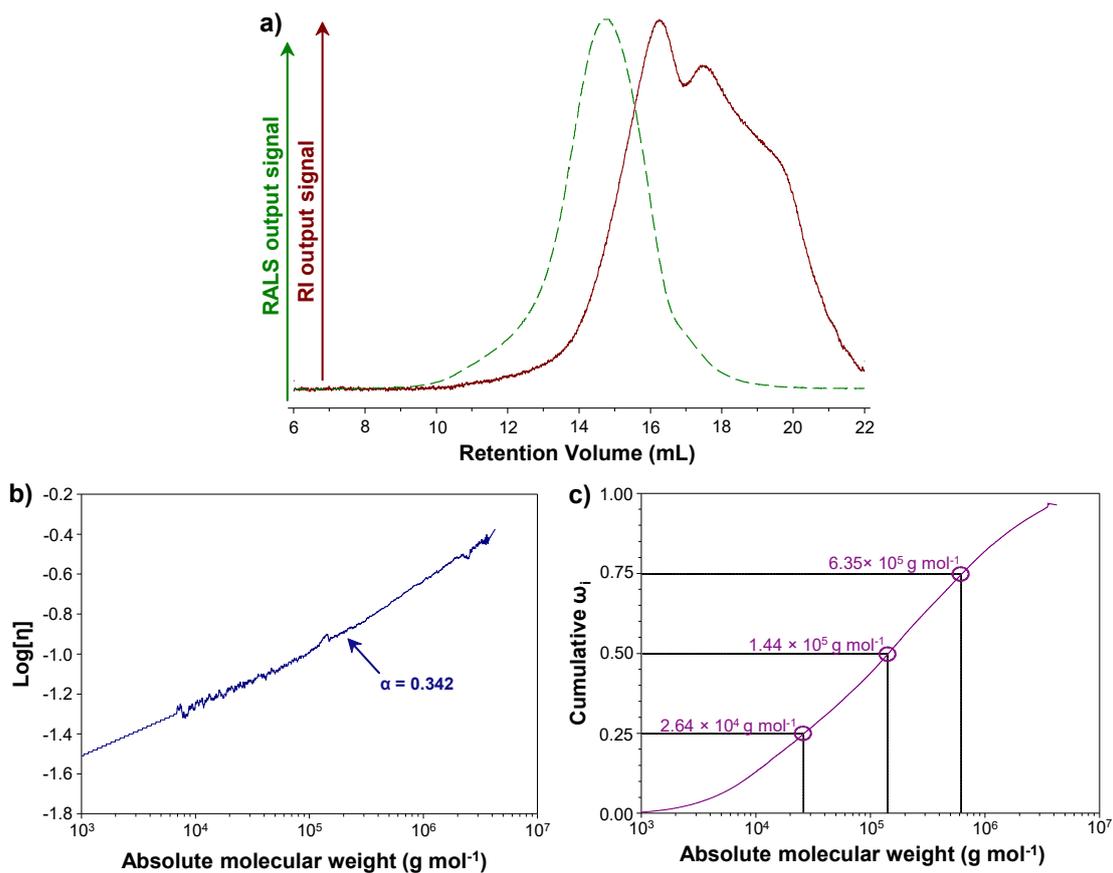


Figure S13 TD-SEC analysis of *p*(*t*BuBzM-EGDMA). a) Overlaid RI (red solid line) and RALS (green dashed line) chromatograms. b) Evaluation of polymer topological structure *via* MHS analysis. c) Analysis of the relationship between absolute molecular weight and the cumulative weight fraction.

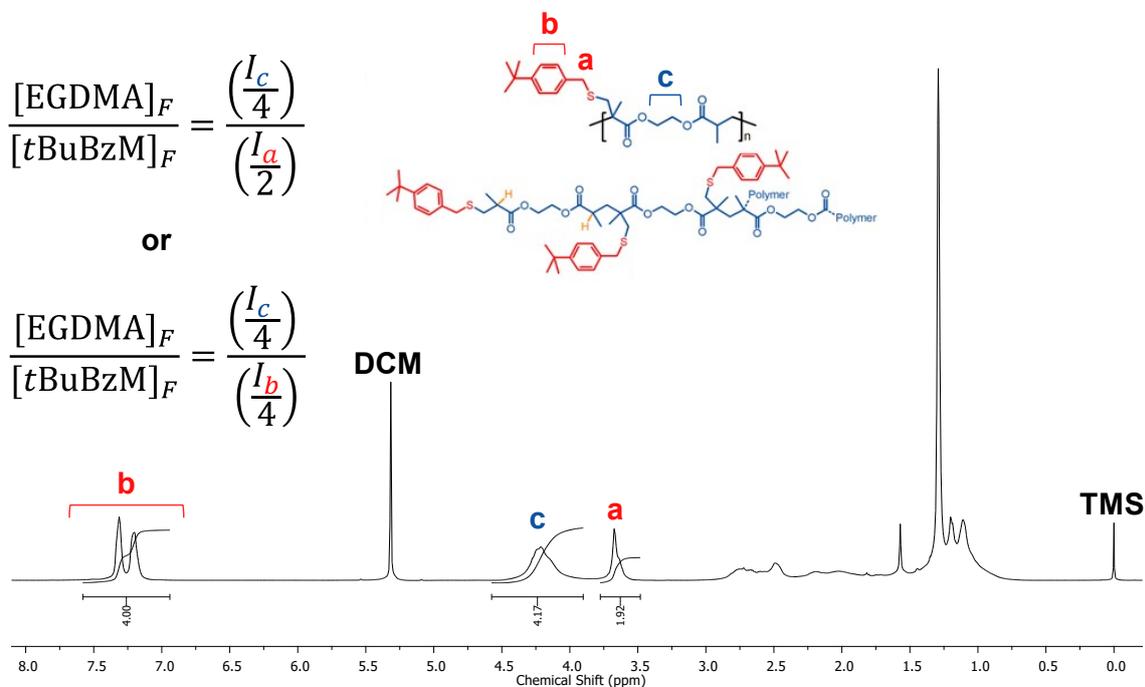


Figure S14 ^1H NMR spectrum (400 MHz, $\text{DCM-}d_2$) of *p*(*t*BuBzM-EGDMA) showing the calculations used to determine the final ratio of EGDMA to *t*BuBzM in the purified polymer ($[\text{EGDMA}]_F/[\text{tBuBzM}]_F$)

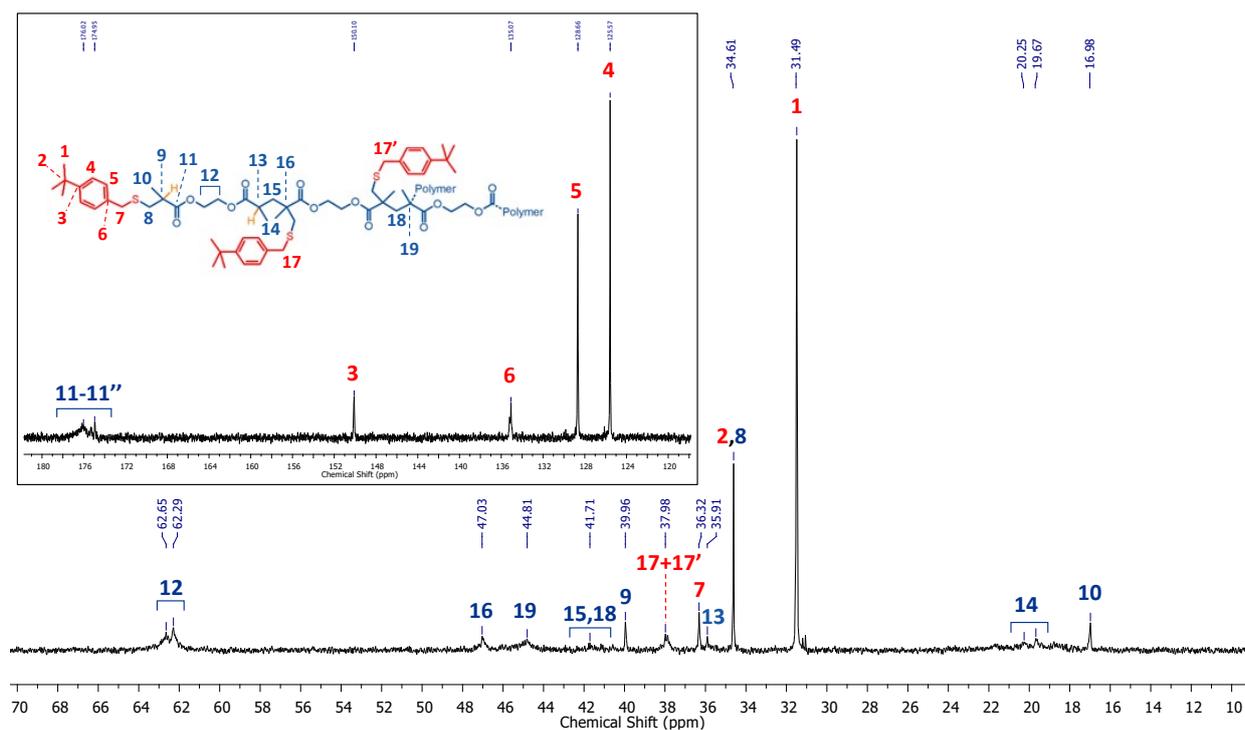


Figure S15 ^{13}C NMR (100 MHz, CDCl_3) spectrum of $p(t\text{BuBzM-EGDMA})$ including assignment of ^{13}C environments.

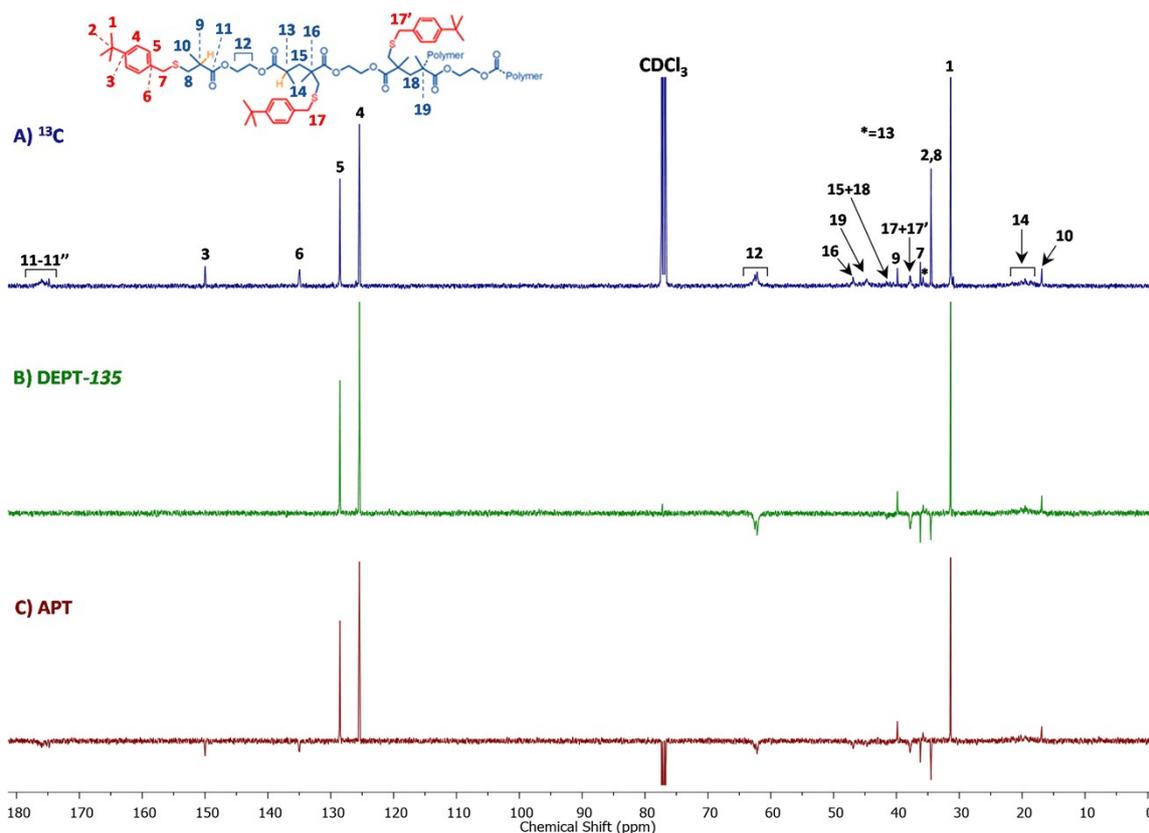


Figure S16 Overlaid A) ^{13}C , B) DEPT-135 and C) APT NMR (100 MHz, CDCl_3) spectra obtained from $p(t\text{BuBzM-EGDMA})$, including assignment of ^{13}C environments.

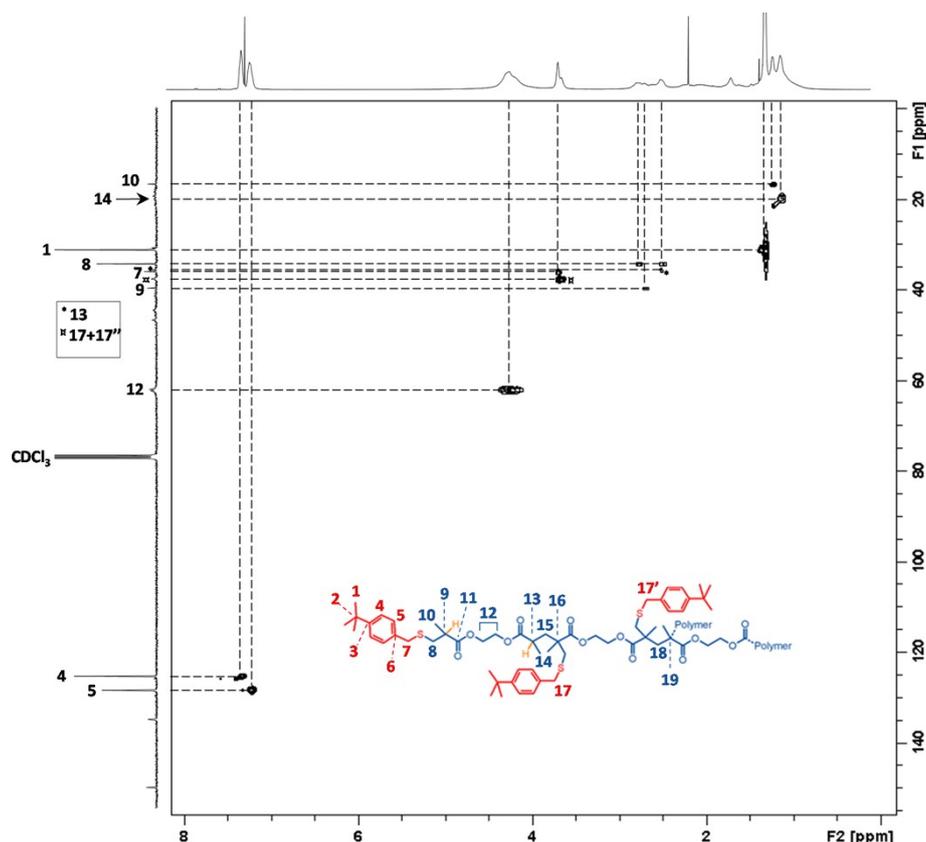


Figure S17 HSQC correlation of ^1H and ^{13}C NMR spectra obtained for $p(t\text{BuBzM-EGDMA})$, enabling assignment of several ^1H and ^{13}C environments.

2.3 Synthesis & characterisation of $p(\text{DDT-BPADMA})$

Bisphenol A dimethacrylate (5.00 g, 13.7 mmol, 0.400 equiv.), DDT (6.94 g, 34.3 mmol, 1.00 equiv.) and AIBN (0.068 g, 0.412 mmol) were placed into a 25 mL round-bottom flask. Toluene (50 wt % based on BPADMA and DDT; 12.01 g, 13.85 mL) was added and the solution was deoxygenated using a nitrogen purge under magnetic stirring for 30 minutes. An aliquot ($\sim 100\ \mu\text{L}$) of the mixture was taken for determination of the molar ratio of BPADMA to DDT prior to initiation ($[\text{BPADMA}]_0/[\text{DDT}]_0$) by ^1H NMR (Figure S19). The flask was then placed in an oil bath at $100\ ^\circ\text{C}$ for 24 hours. The reaction was stopped *via* cooling and exposure to air. An aliquot ($\sim 100\ \mu\text{L}$) of the reaction mixture was taken for determination of monomer conversion *via* ^1H NMR (Figure S20). The reaction mixture was then diluted in THF and precipitated (twice) into methanol (using a good solvent: anti-solvent volume ratio of 1:20) at ambient temperature, yielding a white precipitate. The polymer was dried *in vacuo* at $40\ ^\circ\text{C}$ overnight to yield $p(\text{DDT-BPADMA})$ as a white powder. The product was analysed by TD-SEC (Figure S18) and several ^1H and ^{13}C NMR spectroscopic techniques (Figure S19-S22).

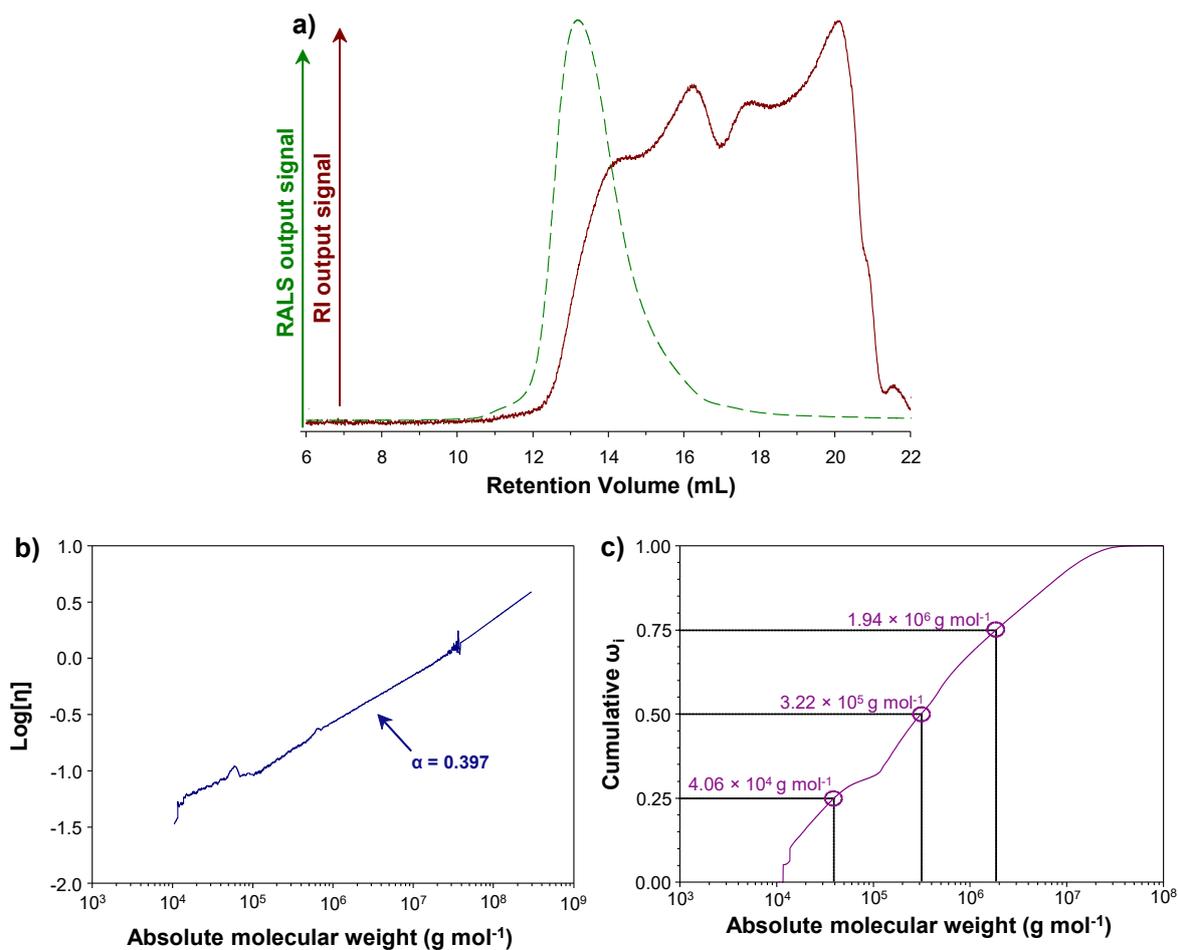


Figure S18 TD-SEC analysis of *p*(DDT-BPDMA). a) Overlaid RI (red solid line) and RALS (green dashed line) chromatograms. b) Evaluation of copolymer topological structure *via* MHS analysis. c) Analysis of the relationship between absolute molecular weight and the cumulative weight fraction.

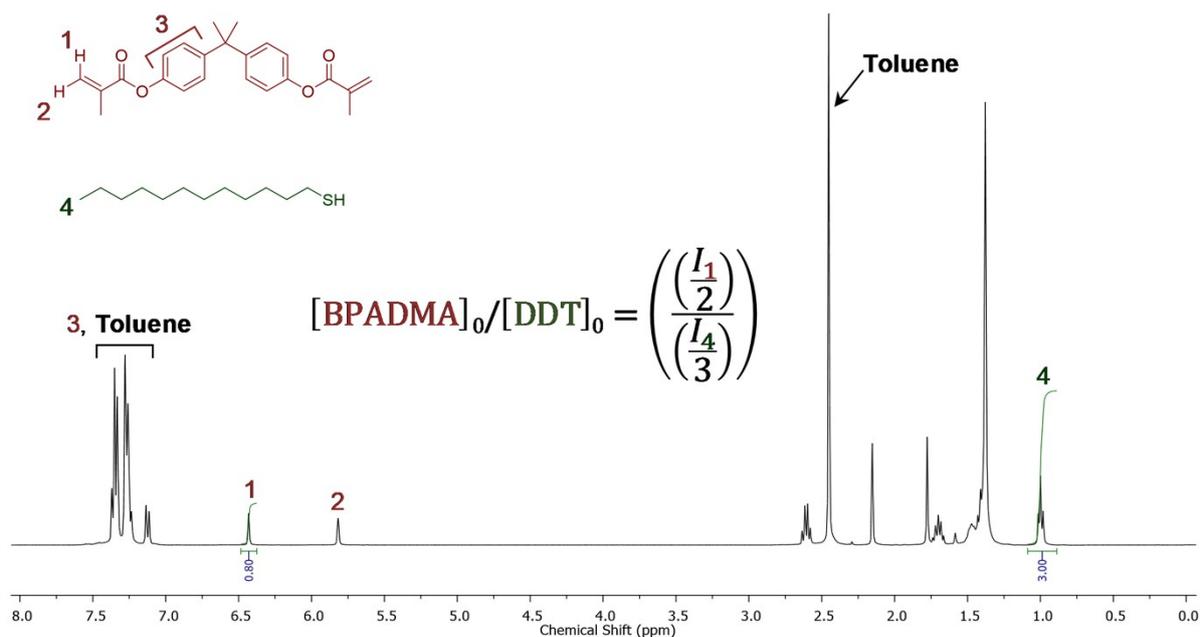


Figure S19 ^1H NMR (400 MHz, CDCl_3) spectrum obtained from the homopolymerisation of BPADMA with DDT prior to thermal initiation ($t = 0$). The equation provided was used to determine the initial ratio of BPADMA to DDT ($[\text{BPADMA}]_0/[\text{DDT}]_0$).

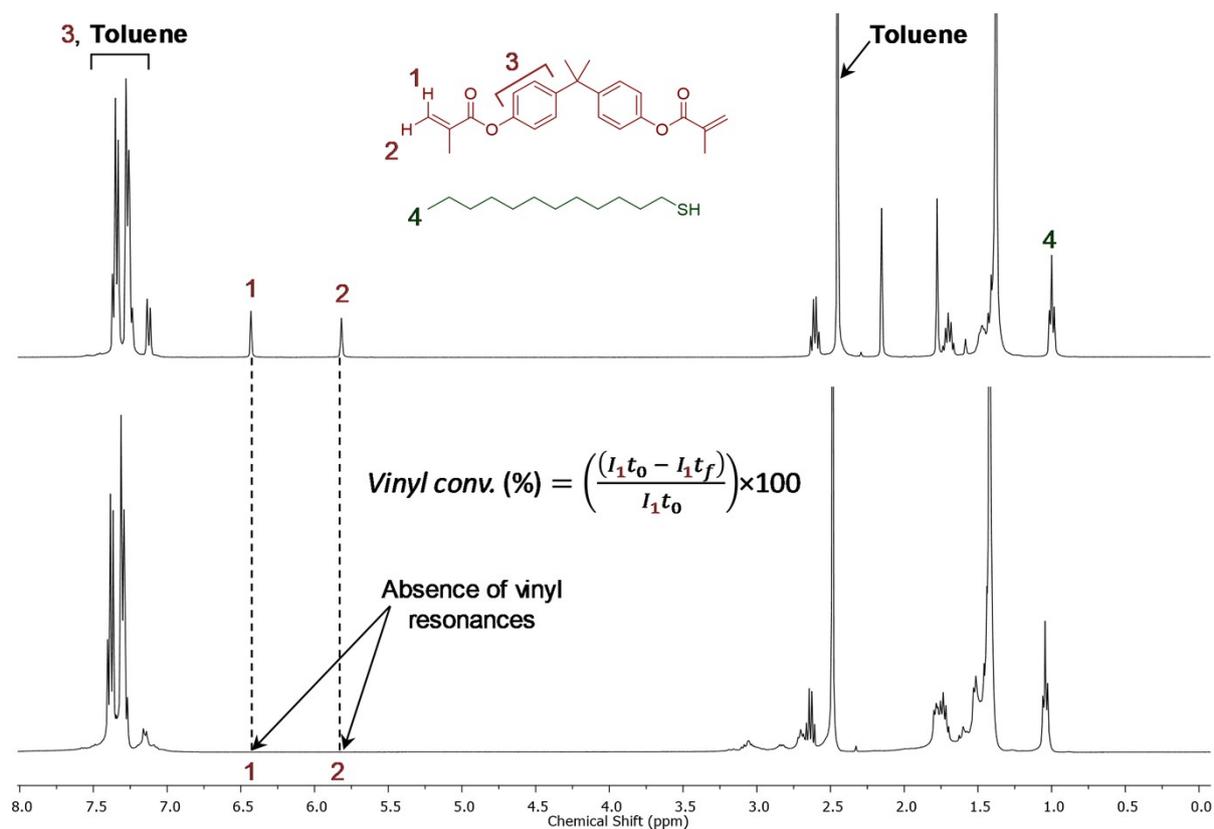


Figure S20 Overlaid ^1H NMR (400 MHz, CDCl_3) spectra obtained from the homopolymerisation of BPADMA with DDT prior to thermal initiation (top) and 24 hours after initiation (bottom). The equation provided was used to determine monomer conversion (integrals normalised with respect to 4).

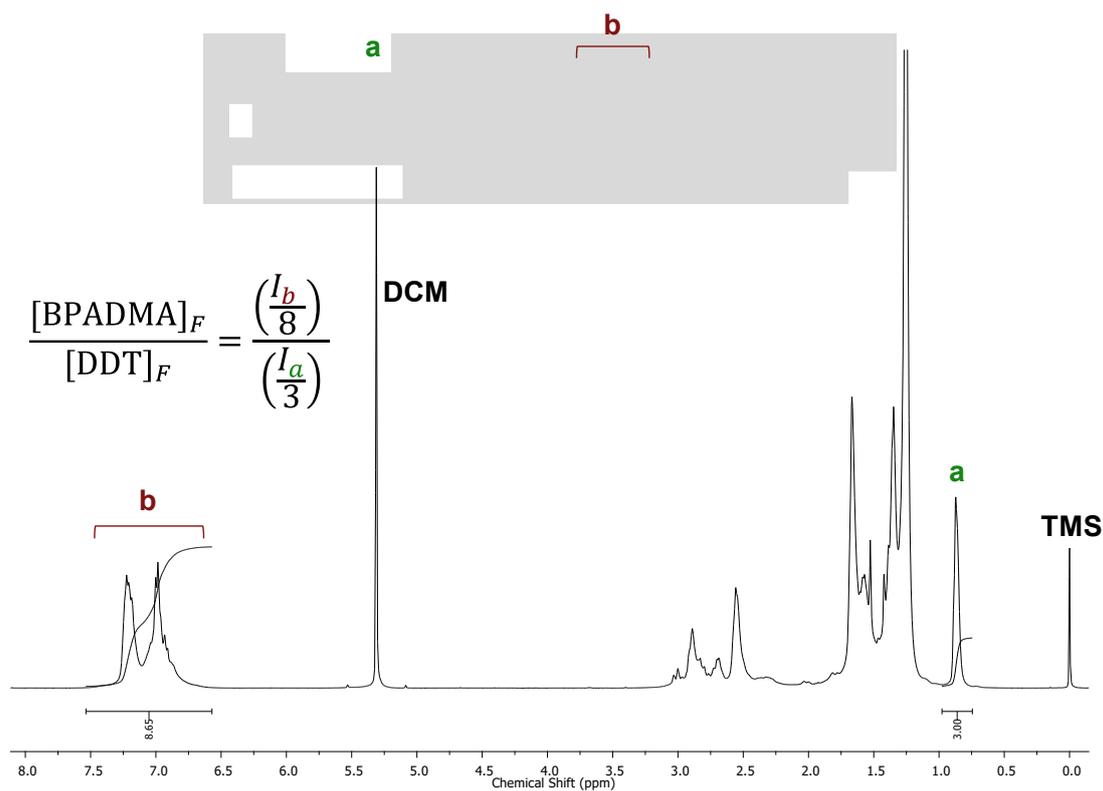


Figure S21 ^1H NMR spectrum (400 MHz, $\text{DCM-}d_2$) of $p(\text{DDT-BPADMA})$ showing the calculations used to determine the final ratio of BPADMA to DDT in the purified polymer ($[\text{BPADMA}]_F/[\text{tBuBzM}]_F$).

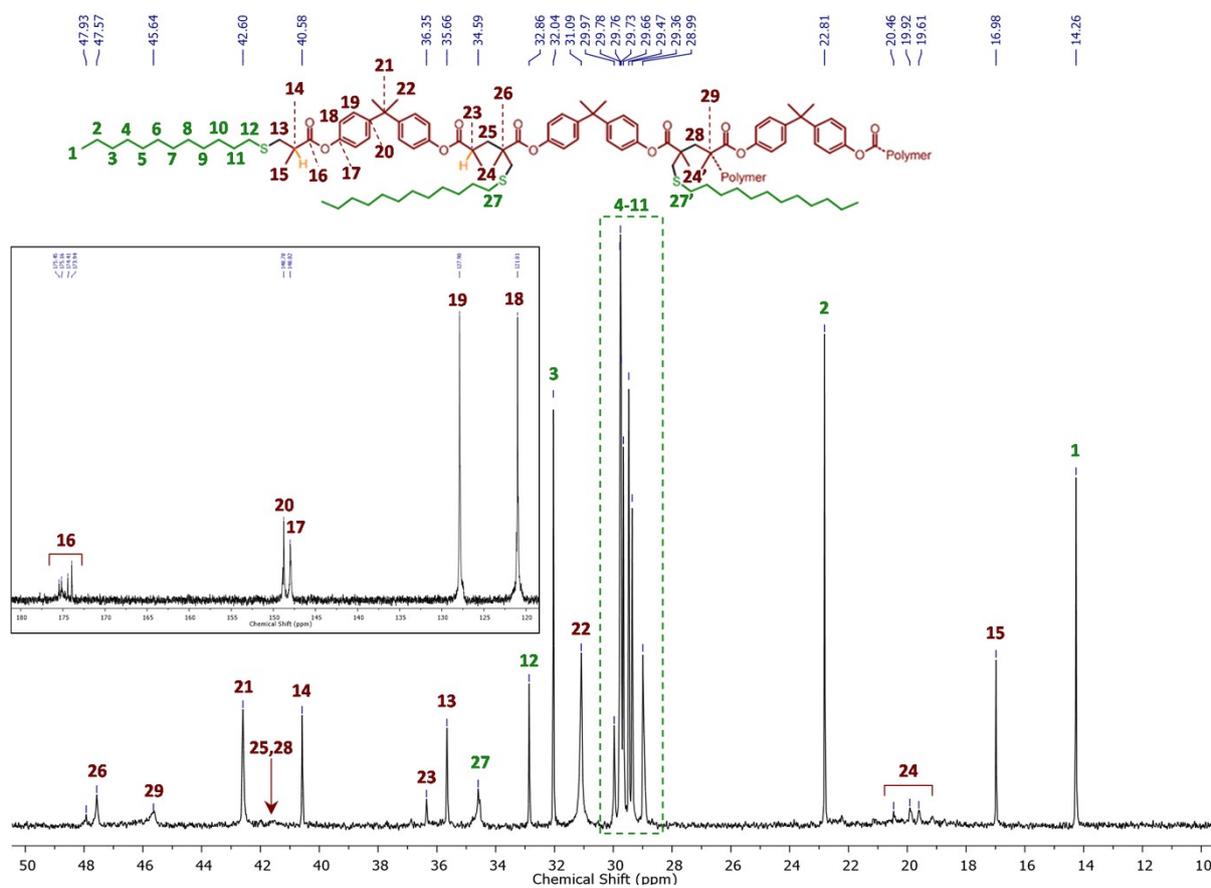


Figure S22 ^{13}C NMR (100 MHz, CDCl_3) spectrum of $p(\text{DDT-BPADMA})$ including assignment of ^{13}C environments.

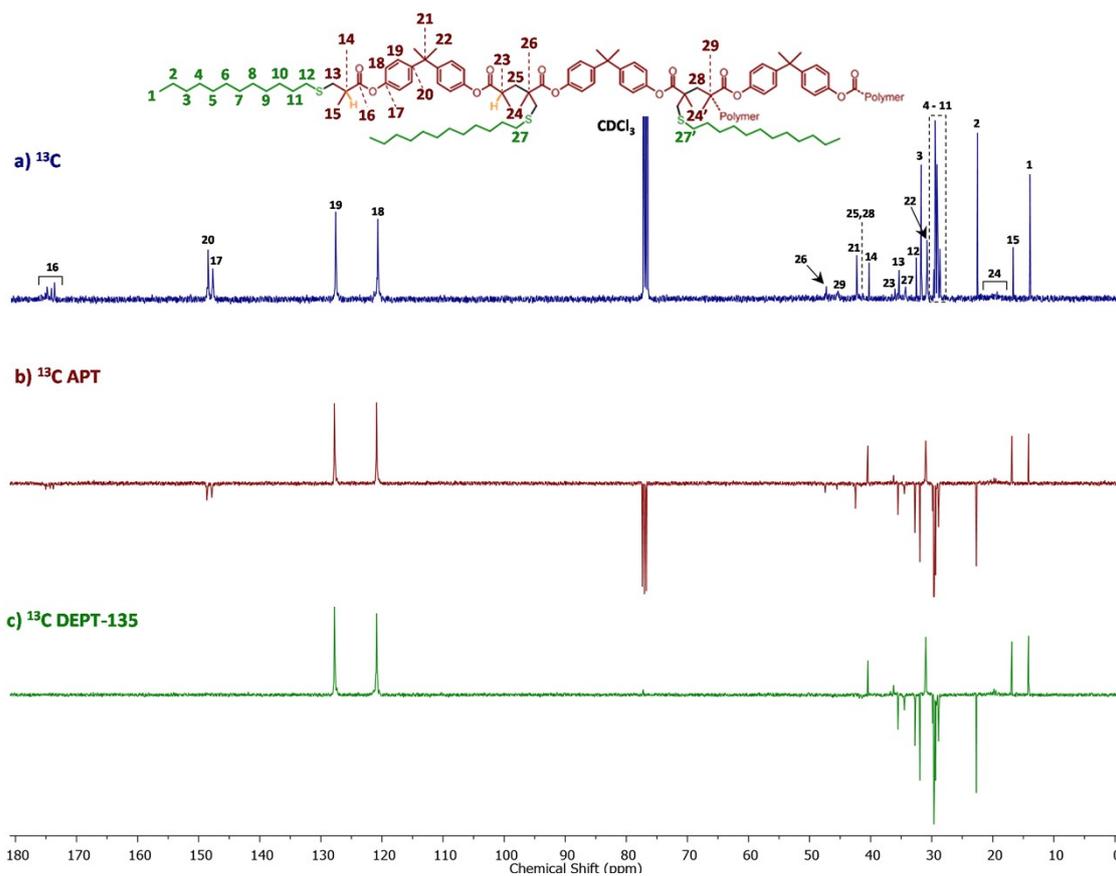


Figure S23 Overlaid A) ¹³C, B) DEPT-135 and C) APT NMR (100 MHz, CDCl₃) spectra obtained from *p*(DDT-BPADMA) including assignment of ¹³C environments.

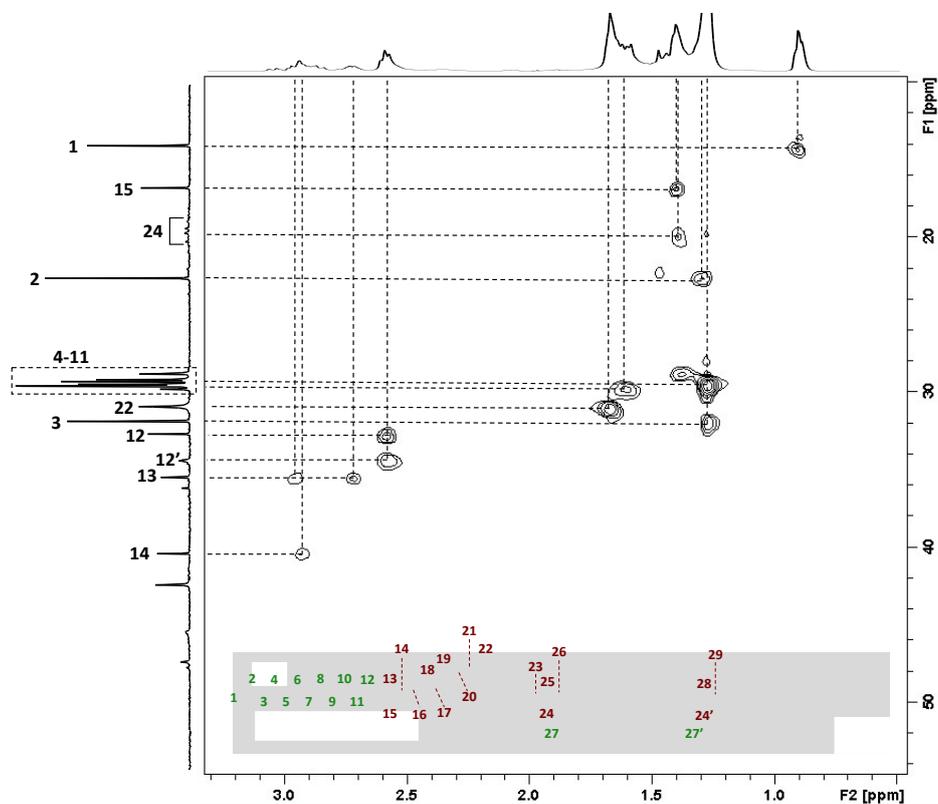


Figure S24 HSQC correlation of ¹H and ¹³C NMR spectra obtained for *p*(DDT-BPADMA), enabling assignment of several ¹H and ¹³C environments.

2.2.4 Synthesis & characterisation of *p*(*t*BuBzM-BPADMA)

BPADMA (5.00 g, 13.7 mmol, 0.425 equiv.), *t*BuBzM (5.82 g, 32.3 mmol, 1.00 equiv.) and AIBN (0.068 g, 0.412 mmol) were placed into a 25 mL round-bottom flask. Toluene (50 wt % based on BPADMA and *t*BuBzM; 10.89 g, 12.56 mL) was added and the solution was deoxygenated using a nitrogen purge under magnetic stirring for 30 minutes. An aliquot (~100 μ L) of the mixture was taken for determination of the molar ratio of BPADMA to *t*BuBzM prior to initiation ($[\text{BPADMA}]_0/[\text{tBuBzM}]_0$) by ^1H NMR (Figure S26). The flask was then placed in an oil bath at 100 $^\circ\text{C}$ for 24 hours. The reaction was stopped *via* cooling and exposure to air. An aliquot (~100 μ L) of the reaction mixture was taken for determination of monomer conversion *via* ^1H NMR (Figure S27). The reaction mixture was then diluted in THF and precipitated into methanol (using a good solvent: anti-solvent volume ratio of 1:20) at ambient temperature, yielding a white precipitate. The polymer was then dried *in vacuo* at 40 $^\circ\text{C}$ overnight to yield *p*(*t*BuBzM-BPADMA) as a white powder. The product was analysed by TD-SEC (Figure S25) and several ^1H and ^{13}C NMR spectroscopic techniques (Figure S26-S29).

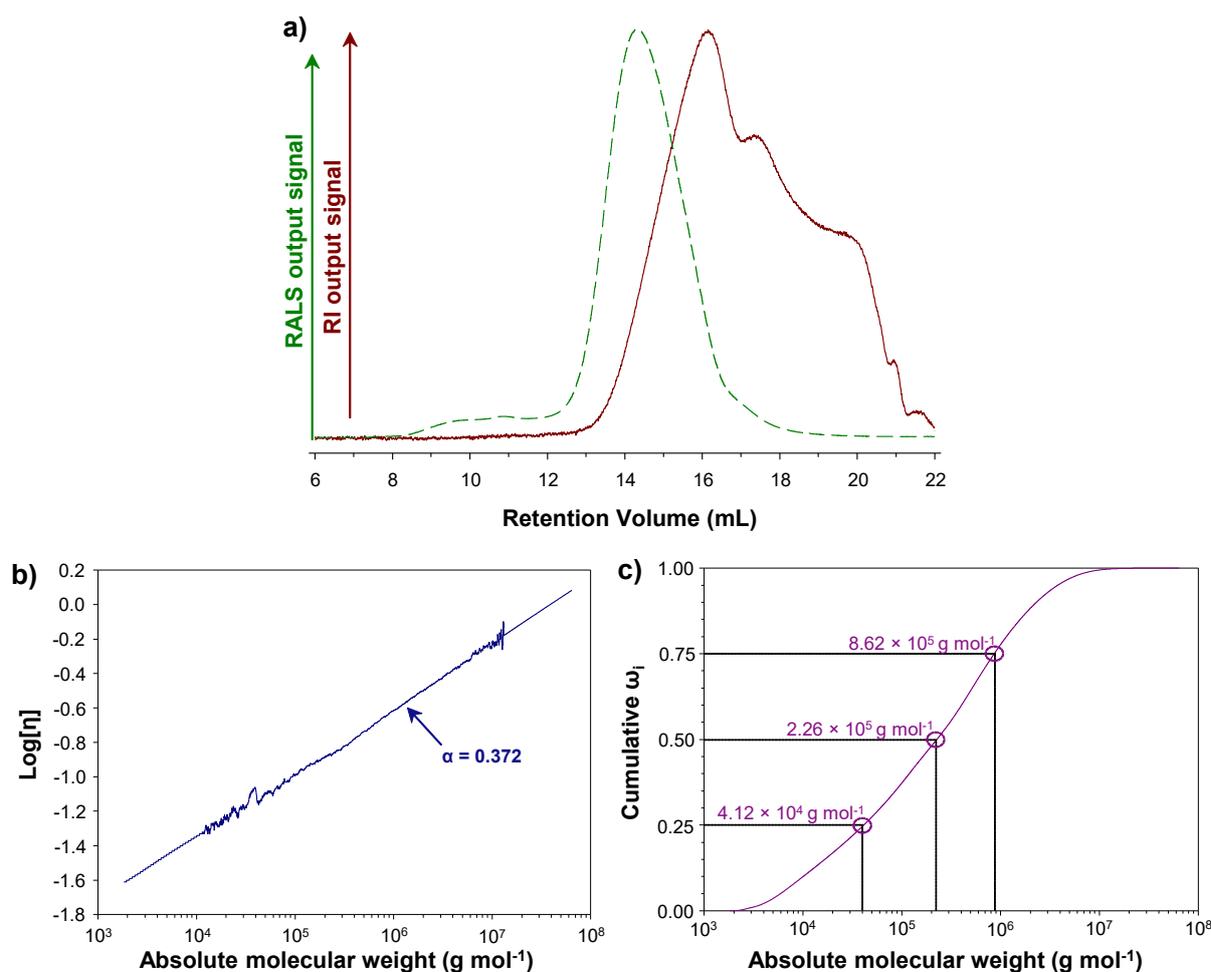


Figure S25 TD-SEC analysis of *p*(*t*BuBzM-BPADMA). a) Overlaid RI (red solid line) and RALS (green dashed line) chromatograms. b) Evaluation of polymer topological structure *via* MHS. c) Analysis of the relationship between absolute molecular weight and the cumulative weight fraction.

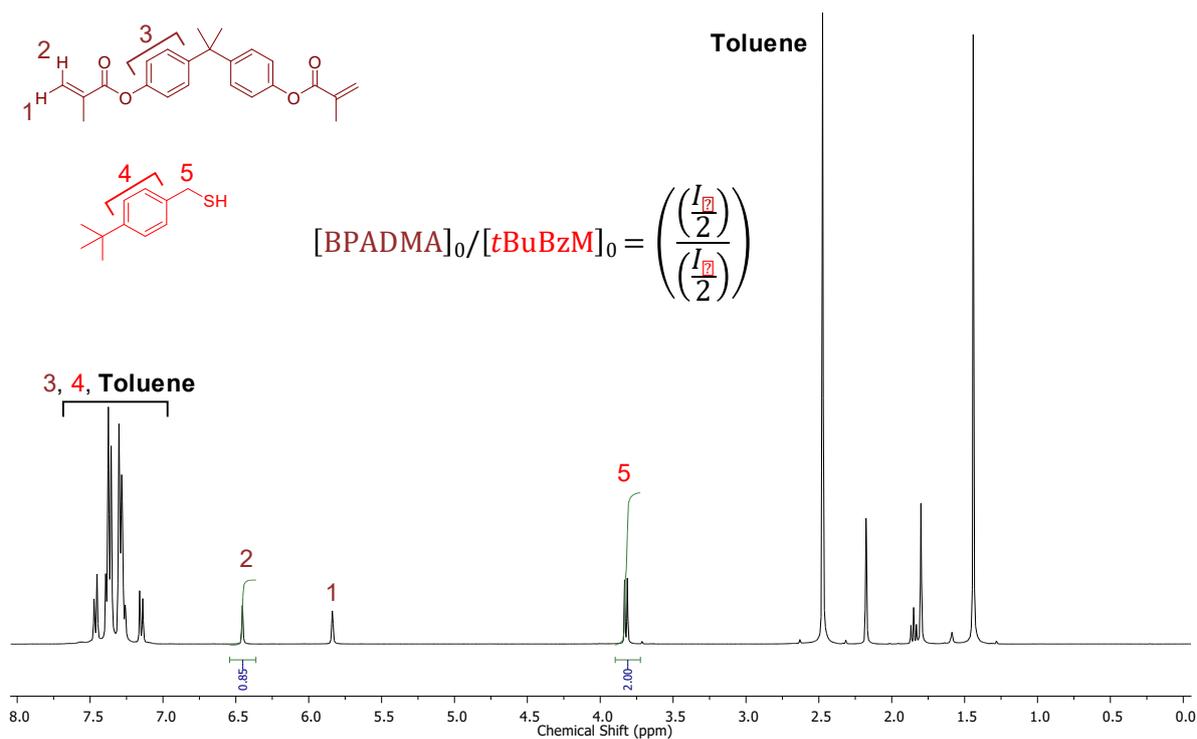


Figure S26 ^1H NMR (400 MHz, CDCl_3) spectrum obtained from the homopolymerisation of BPADMA with $t\text{BuBzM}$ prior to thermal initiation ($t = 0$). The equation provided was used to determine the initial ratio of BPADMA to $t\text{BuBzM}$ ($[\text{BPADMA}]_0/[\text{tBuBzM}]_0$).

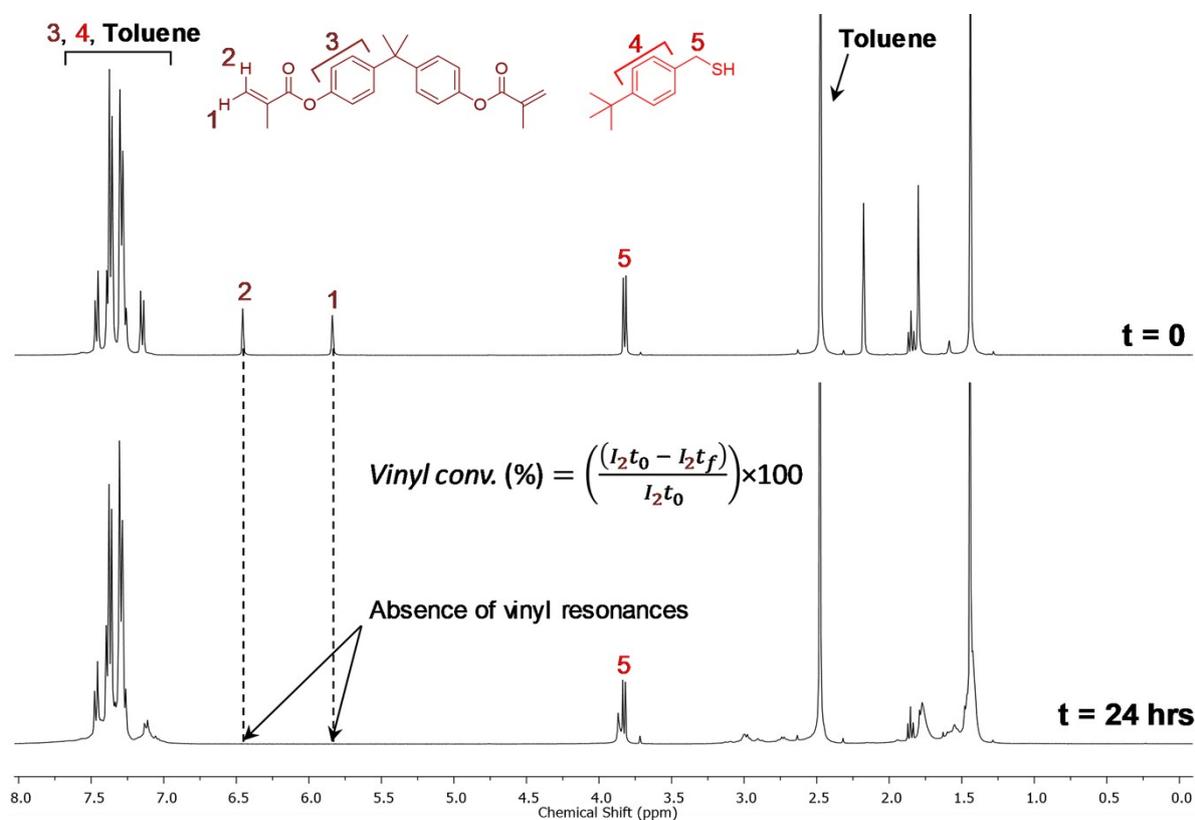


Figure S27 Overlaid ^1H NMR (400 MHz, CDCl_3) spectra obtained from the homopolymerisation of BPADMA with $t\text{BuBzM}$ prior to thermal initiation (top) and 24 hours after initiation (bottom). The equation provided was used to determine monomer conversion (integrals normalised with respect to 5).

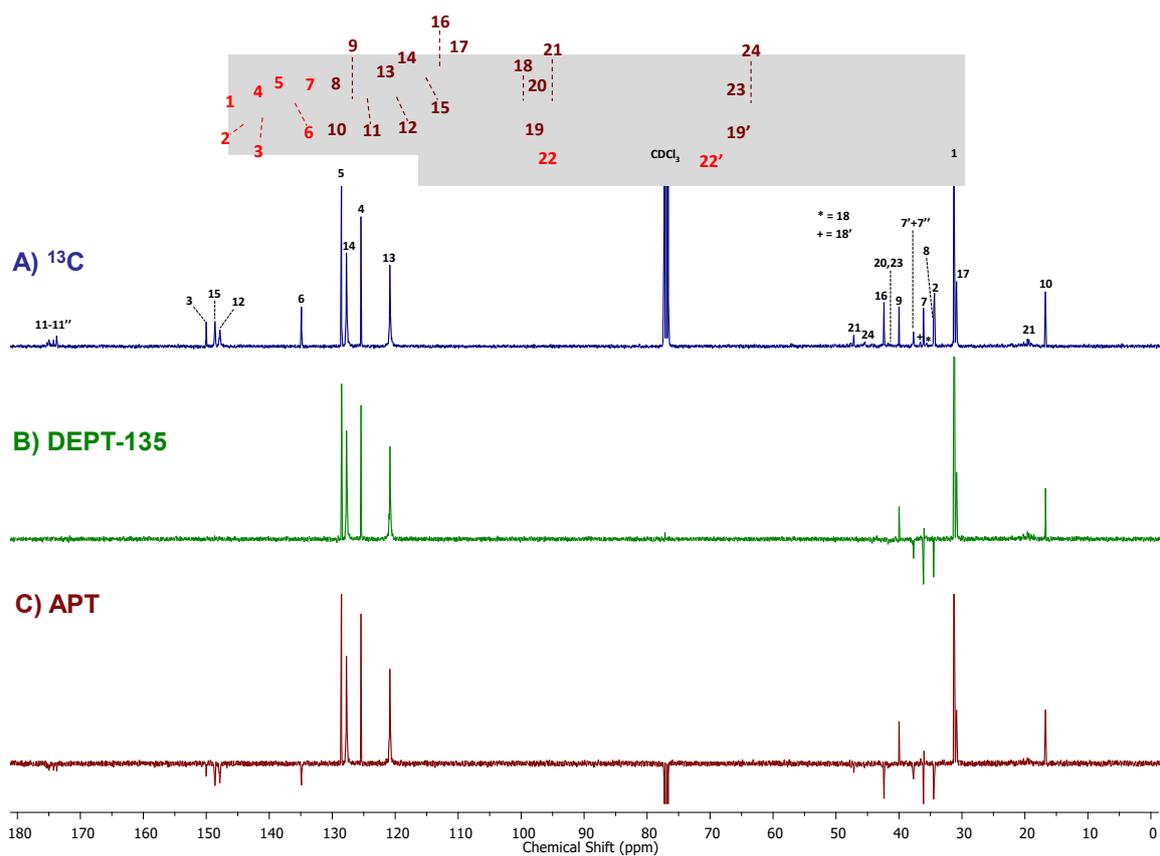


Figure S30 Overlaid A) ¹³C, B) DEPT-135 and C) APT NMR (100 MHz, CDCl₃) spectra obtained from *p*(*t*BuBzM-BPADMA) including assignment of ¹³C environments.

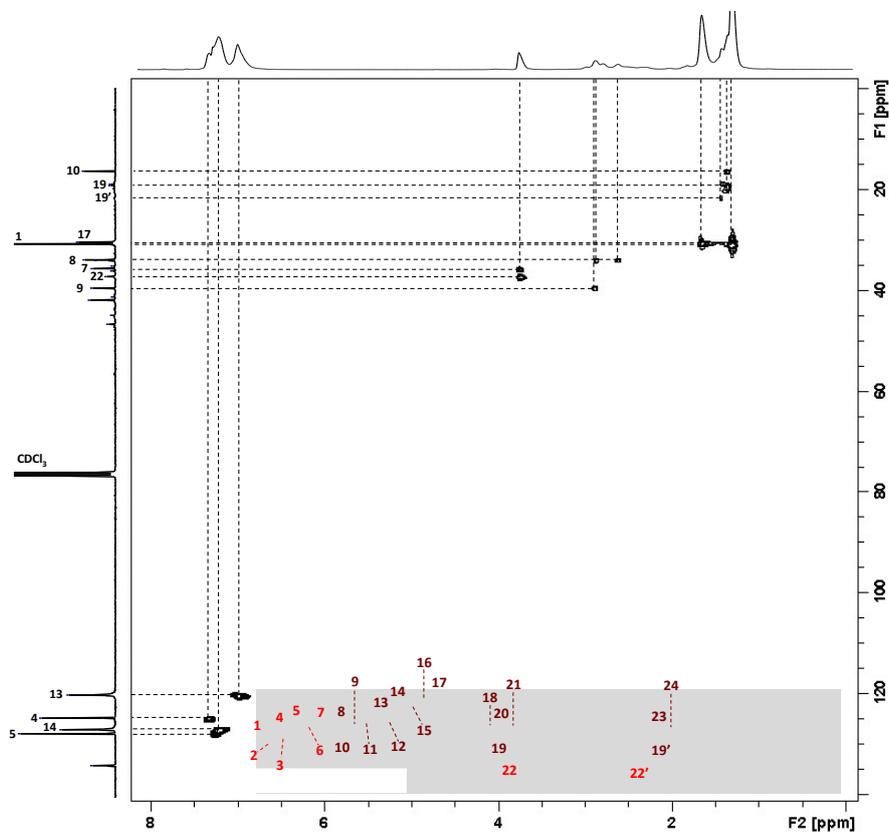


Figure S31 HSQC correlation of ¹H and ¹³C NMR spectra obtained for *p*(*t*BuBzM-BPADMA), enabling assignment of several ¹H and ¹³C environments.

2.2.5 Synthesis & characterisation of *p*([*t*BuBzM-EGDMA]-*stat*-[DDT-EGDMA])

EGDMA (5.00 g, 25.2 mmol, 0.825 equiv.), *t*BuBzM (2.76 g, 15.3 mmol, 0.500 equiv.), DDT (3.09 g, 15.3 mmol, 0.500 equiv.) and AIBN (0.124 g, 0.756 mmol) were placed into a 25 mL round-bottom flask. Ethyl acetate (50 wt % based on EGDMA, *t*BuBzM and DDT; 10.98 g, 12.17 mL) was added and the solution was deoxygenated using a nitrogen purge under magnetic stirring for 30 minutes. An aliquot (~100 μ L) of the mixture was taken for determination of the initial molar ratios of: (i) multi-vinyl taxogen (MVT) to total telogen ($[MVT]_0/\Sigma[Te]_0$) and (ii) the composition of the telogen mixture ($[tBuBzM]_0/\Sigma[Te]_0$) by 1H NMR analysis (Figure S32). The flask was then placed in an oil bath at 70 $^{\circ}C$ for 24 hours. The reaction was stopped *via* cooling and exposure to air. An aliquot (~100 μ L) of the reaction mixture was taken for determination of monomer conversion *via* 1H NMR (Figure S33). The reaction mixture was then diluted in THF and precipitated into methanol (using a good solvent: anti-solvent volume ratio of 1:20) at ambient temperature, yielding a white precipitate. The polymer was dried *in vacuo* at 40 $^{\circ}C$ overnight to yield *p*([*t*BuBzM-EGDMA]-*stat*-[DDT-EGDMA]) as a white powder. The product was analysed by TD-SEC (Figure S34) and several 1H and ^{13}C NMR spectroscopic techniques (Figure S35-S40).

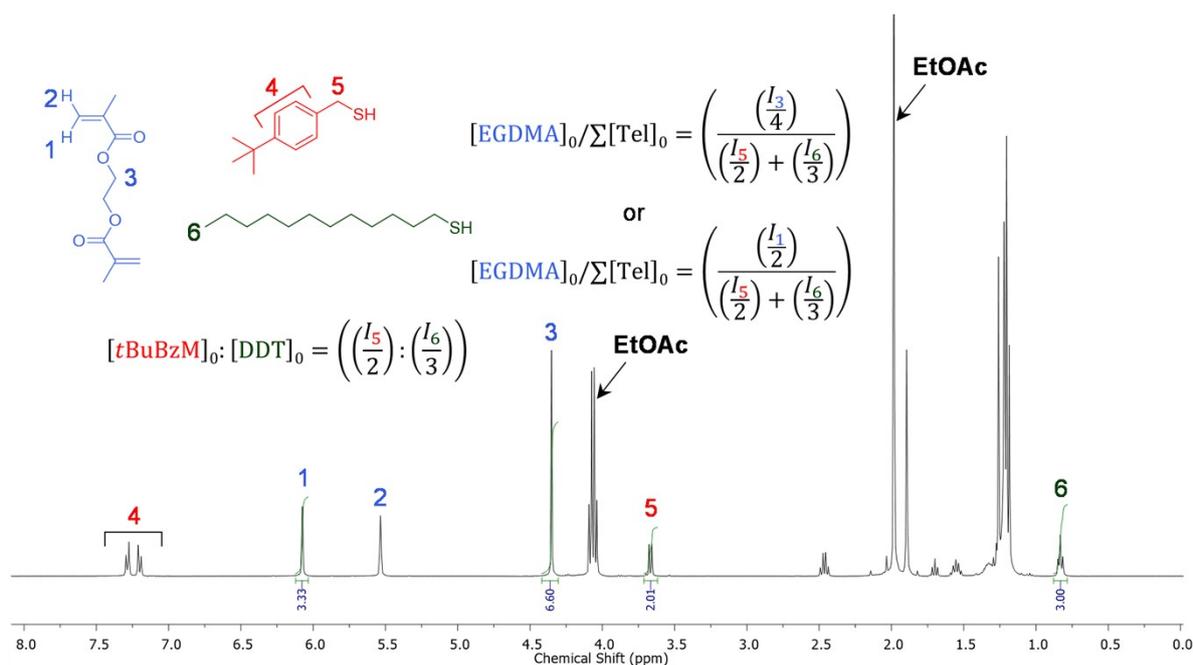


Figure S32 1H NMR (400 MHz, $CDCl_3$) spectrum obtained from the mixed telogen copolymerisation of DDT and *t*BuBzM with EGDMA prior to thermal initiation ($t = 0$). The equations used to determine the initial ratio of EGDMA to telogen ($[EGDMA]_0/\Sigma[Te]_0$) and the composition of the telogen mixture ($[tBuBzM]_0:[DDT]_0$) are provided.

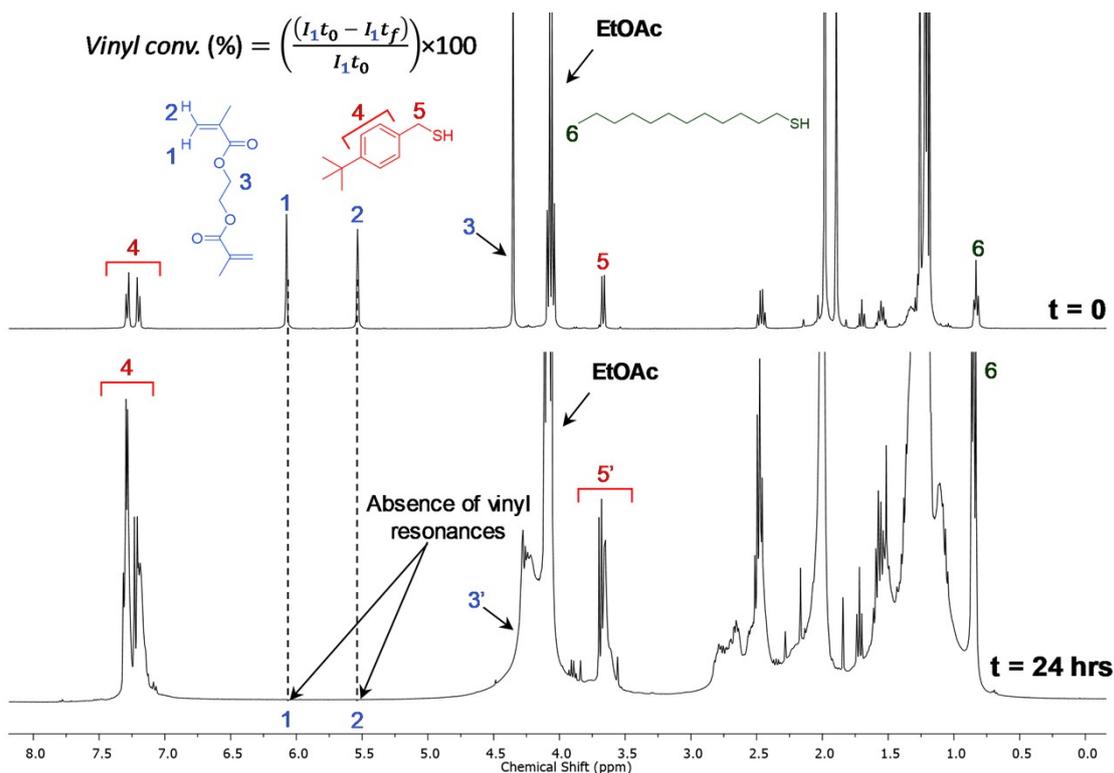


Figure S33 Overlaid ^1H NMR (400 MHz, CDCl_3) spectra obtained from the mixed telogen copolymerisation of DDT and *t*BuBzM with EGDMA prior to thermal initiation (top) and 24 hours after initiation (bottom). The equation provided was used to determine monomer conversion (integrals normalised with respect to 6).

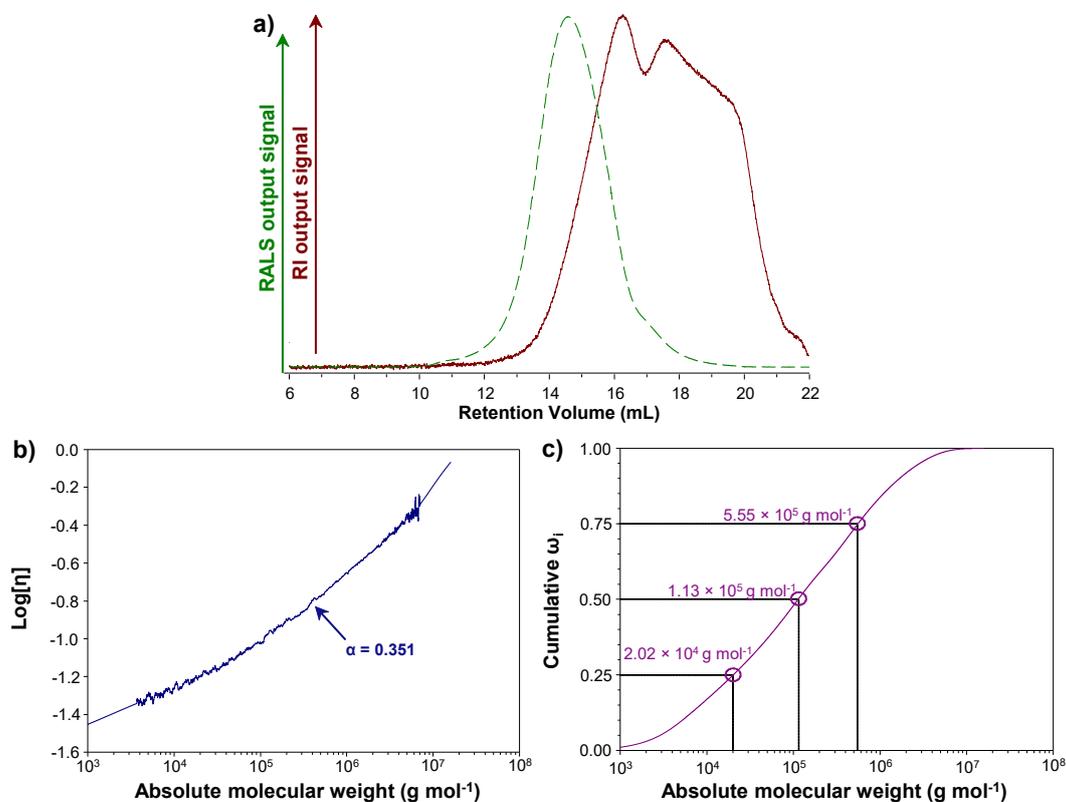


Figure S34 TD-SEC analysis of $p([t\text{BuBzM-EGDMA}]_{\text{stat}}\text{-}[DDT\text{-EGDMA}])$. a) Overlaid RI (red solid line) and RALS (green dashed line) chromatograms. b) Evaluation of copolymer topological structure *via* MHS analysis. c) Analysis of the relationship between absolute molecular weight and the cumulative weight fraction.

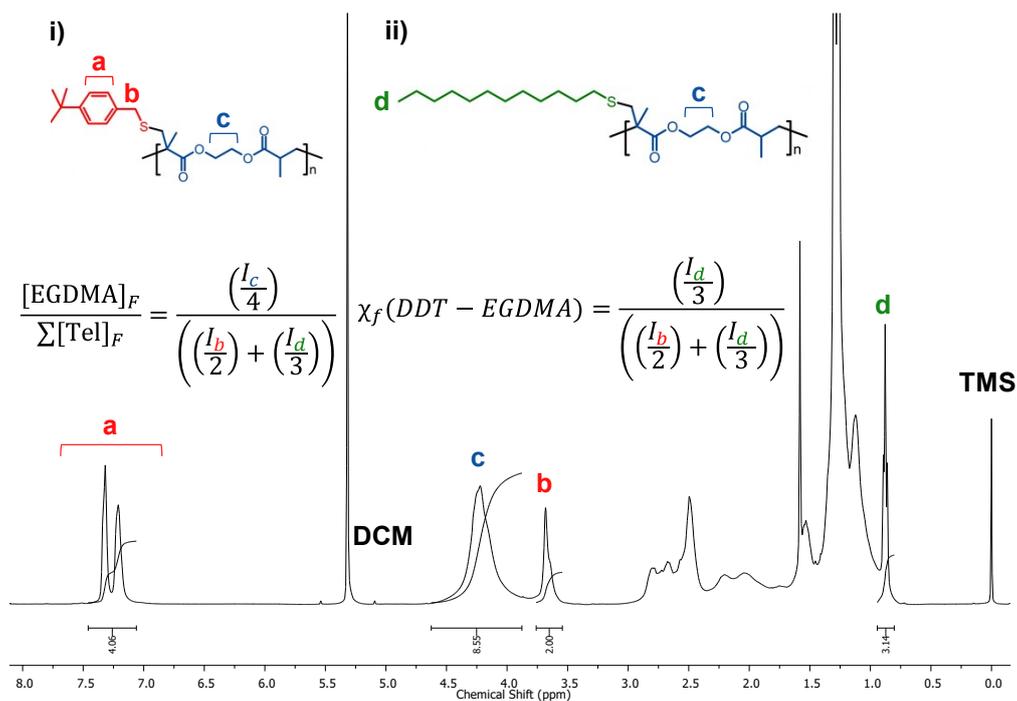


Figure S35 ^1H NMR spectrum (400 MHz, DCM-d_2) of $p([t\text{BuBzM-EGDMA}]\text{-stat-[DDT-EGDMA]})$ showing the calculations used to determine the final ratio of EGDMA to telogen ($[\text{EGDMA}]_F/\Sigma[\text{TeI}]_F$) and the telogen composition (mole fraction, χ_f) in the purified polymer.

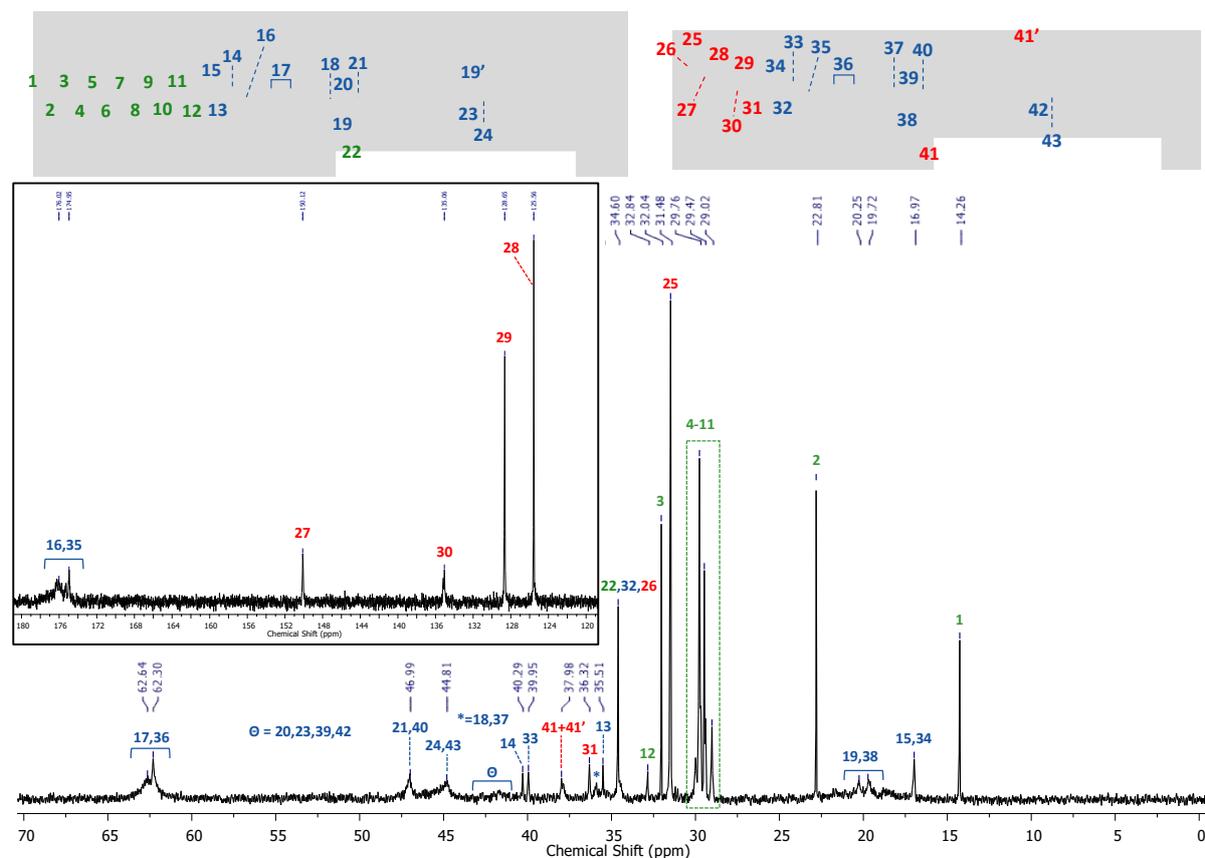


Figure S36 ^{13}C NMR (100 MHz, CDCl_3) spectrum of $p([t\text{BuBzM-EGDMA}]\text{-stat-[DDT-EGDMA]})$ including assignment of ^{13}C environments.

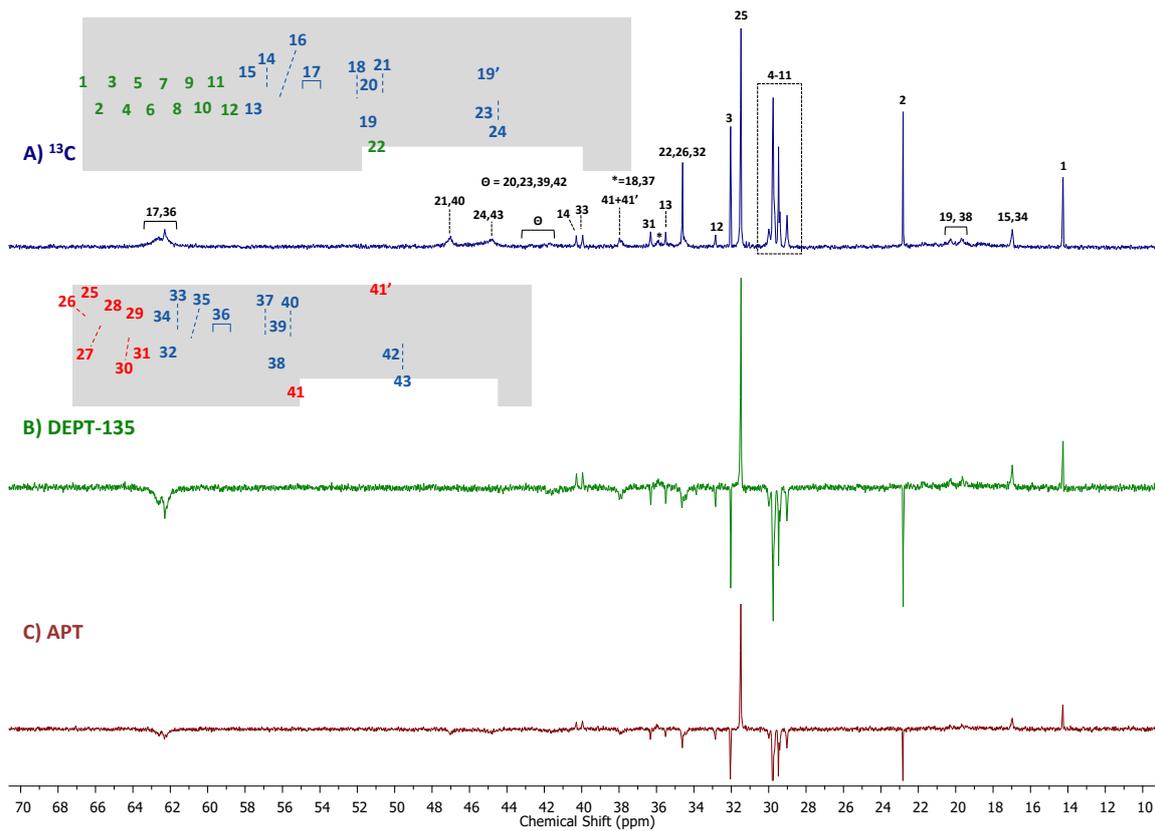


Figure S37 Overlaid A) ^{13}C , B) DEPT-135 and C) APT NMR (100 MHz, CDCl_3) spectra obtained from $p([t\text{BuBzM-EGDMA}]\text{-stat-}[\text{DDT-EGDMA}])$ including assignment of ^{13}C environments.

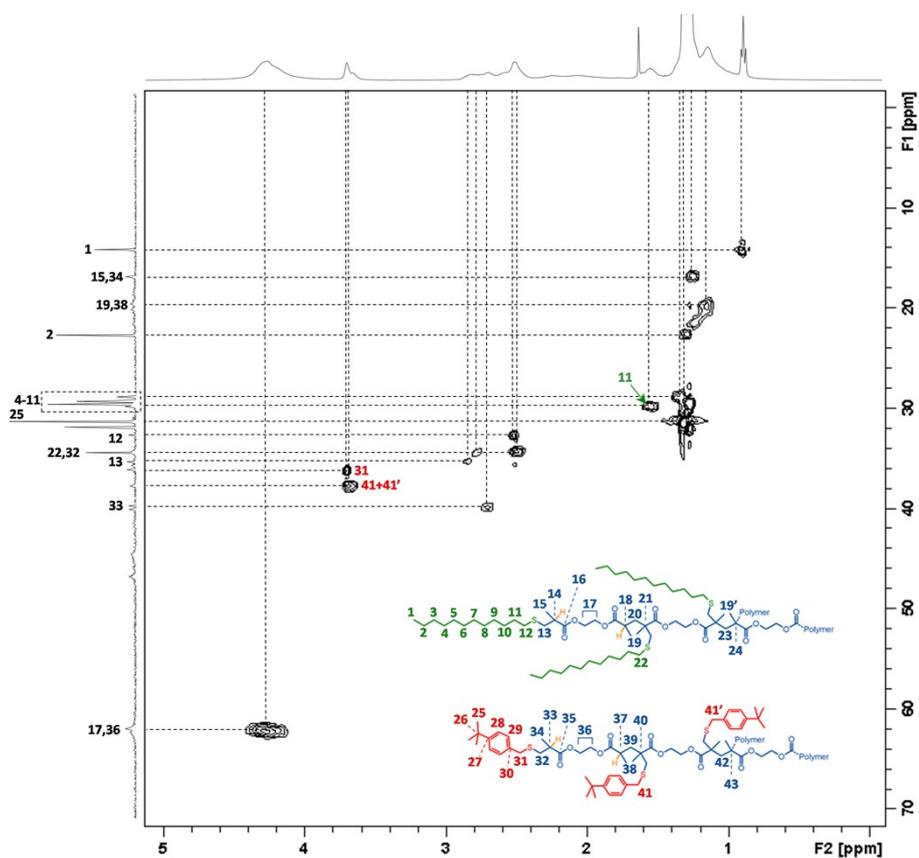


Figure S38 HSQC correlation of ^1H and ^{13}C NMR spectra obtained for $p([t\text{BuBzM-EGDMA}]\text{-stat-}[\text{DDT-EGDMA}])$, enabling assignment of several ^1H and ^{13}C environments.

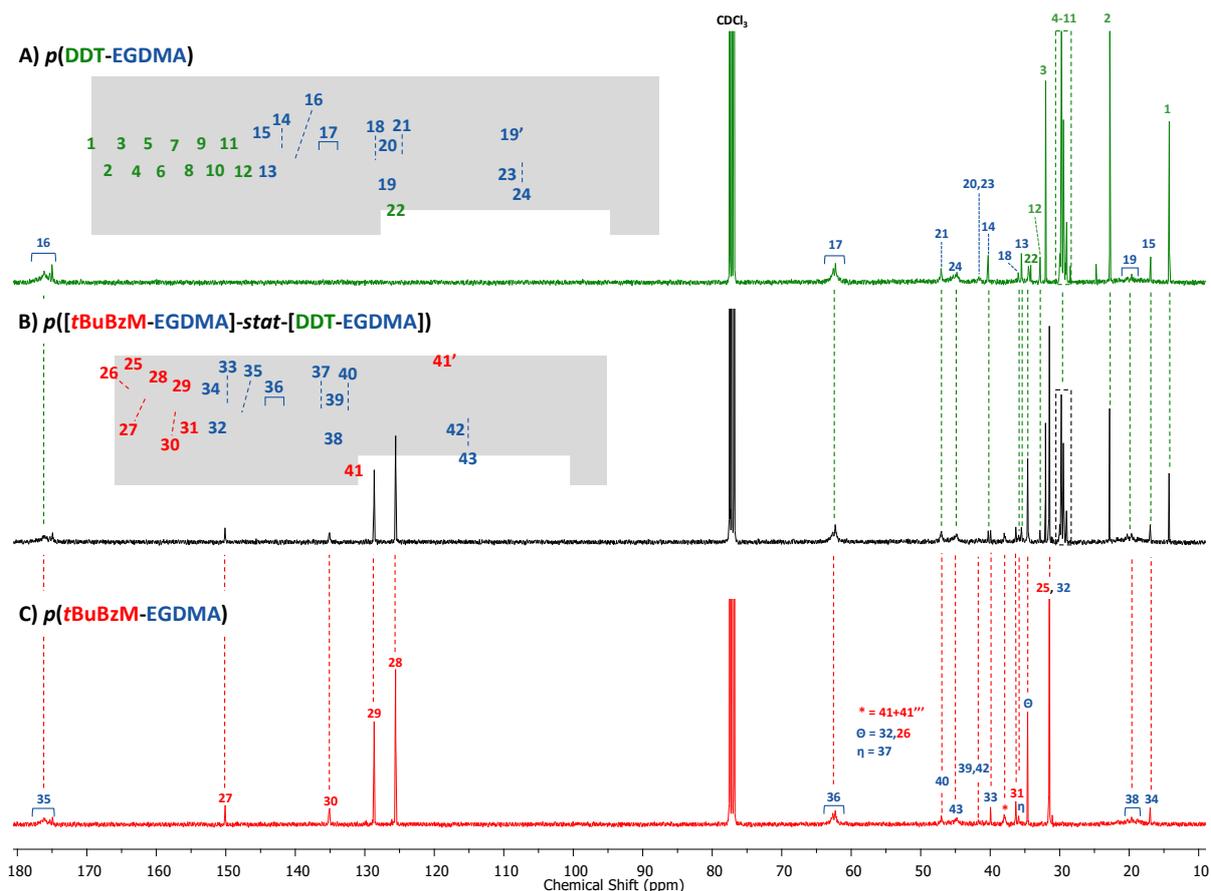


Figure S39 Overlaid ^{13}C NMR spectra (100 MHz, CDCl_3) obtained for A) $p(\text{DDT-EGDMA})$, B) $p([\text{tBuBzM-EGDMA}]\text{-stat-}[\text{DDT-EGDMA}])$ and C) $p(\text{tBuBzM-EGDMA})$. This shows the presence of key structural units from both $p(\text{DDT-EGDMA})$ (green dashed lines) and $p(\text{tBuBzM-EGDMA})$ (red dotted lines) repeat units, within the $p([\text{tBuBzM-EGDMA}]\text{-stat-}[\text{DDT-EGDMA}])$ NMR spectrum.

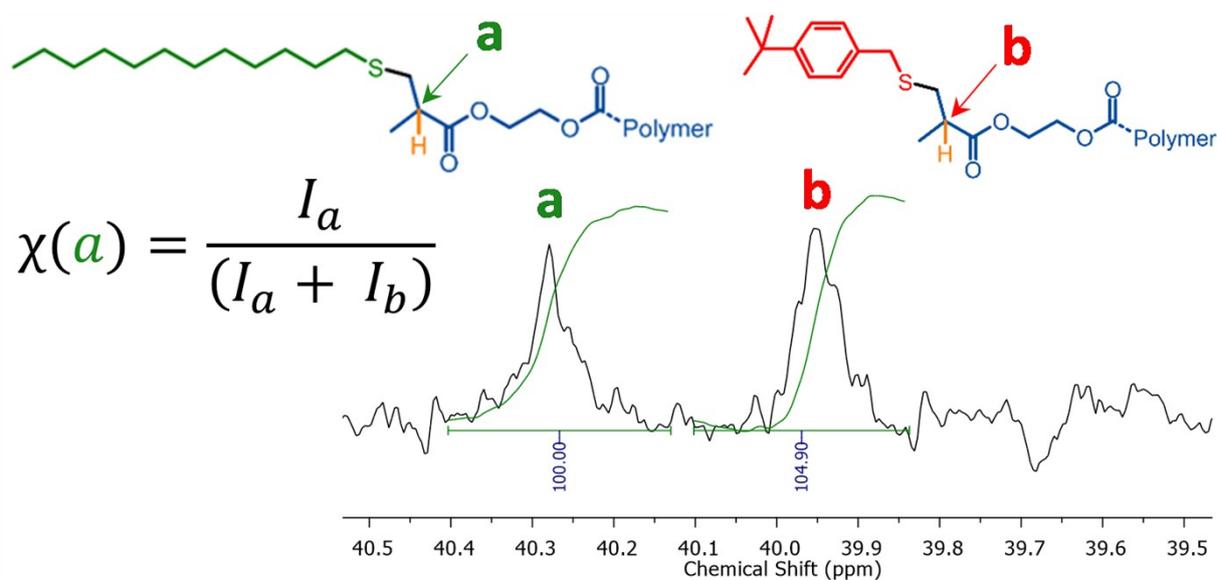


Figure S40 Inverse-gated ^{13}C NMR spectra (100 MHz, CDCl_3) obtained for $p([\text{tBuBzM-EGDMA}]\text{-stat-}[\text{DDT-EGDMA}])$, showing the relative intensities of DP 1 repeat units within the branched copolymer structure.

2.2.6 Synthesis & characterisation of $p([t\text{BuBzM-BPADMA}]\text{-stat-}[\text{DDT-BPADMA}])$

BPADMA (5.00 g, 13.7 mmol, 0.400 equiv.), $t\text{BuBzM}$ (3.09 g, 17.2 mmol, 0.500 equiv.), DDT (3.47 g, 17.2 mmol, 0.500 equiv.) and AIBN (0.068 g, 0.412 mmol) were placed into a 25 mL round-bottom flask. Toluene (50 wt % based on BPADMA, $t\text{BuBzM}$ and DDT; 11.63 g, 13.41 mL) was added and the solution was deoxygenated using a nitrogen purge under magnetic stirring for 30 minutes. An aliquot (~100 μL) of the mixture was taken for determination of the initial molar ratios of: (i) multi-vinyl taxogen (MVT) to total telogen ($[\text{MVT}]_0/\sum[\text{Tel}]_0$) and (ii) the composition of the telogen mixture ($[t\text{BuBzM}]_0/\sum[\text{Tel}]_0$) by ^1H NMR analysis (Figure S41). The flask was then placed in an oil bath at 100 $^\circ\text{C}$ for 24 hours. The reaction was stopped *via* cooling and exposure to air. An aliquot (~100 μL) of the reaction mixture was taken for determination of monomer conversion *via* ^1H NMR (Figure S42). The reaction mixture was then diluted in THF and precipitated into methanol (using a good solvent: anti-solvent volume ratio of 1:20) at ambient temperature, yielding a white precipitate. The polymer was dried *in vacuo* at 40 $^\circ\text{C}$ overnight to yield $p([t\text{BuBzM-BPADMA}]\text{-stat-}[\text{DDT-BPADMA}])$ as a white powder. The product was analysed by TD-SEC (Figure S43) and several ^1H and ^{13}C NMR spectroscopic techniques (Figure S44-S49).

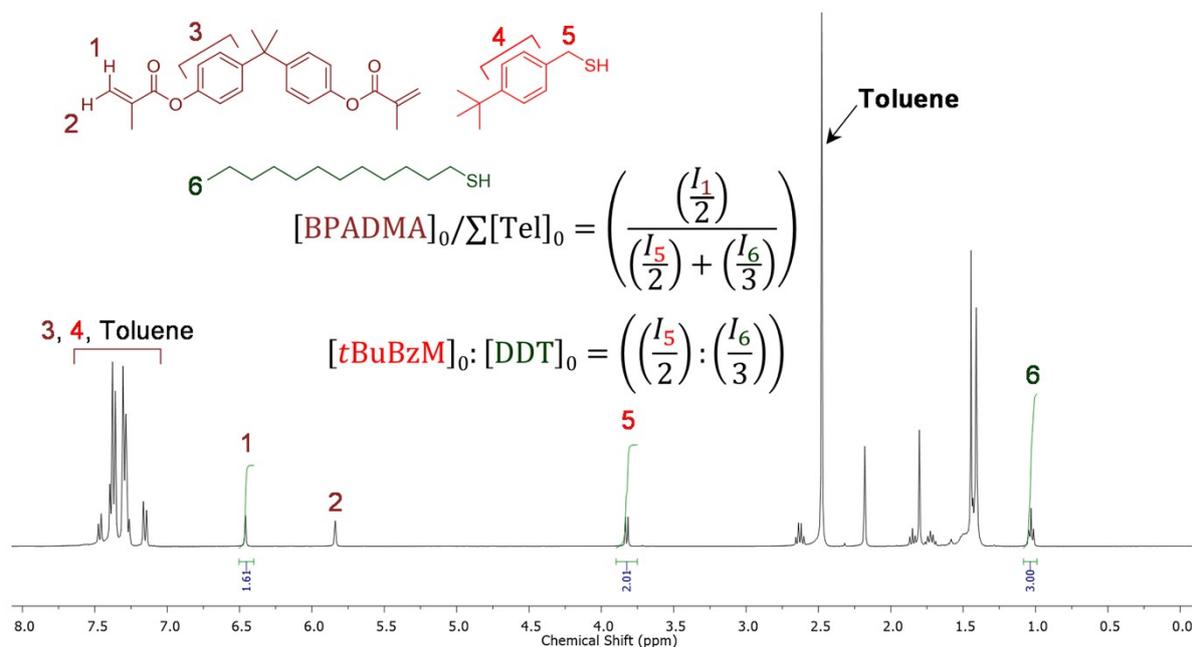


Figure S41 ^1H NMR (400 MHz, CDCl_3) spectrum obtained from the mixed telogen copolymerisation of DDT and $t\text{BuBzM}$ with BPADMA prior to thermal initiation ($t = 0$). The equations used to determine the initial ratio of BPADMA to telogen ($[\text{EGDMA}]_0/\sum[\text{Tel}]_0$) and the composition of the telogen mixture ($[t\text{BuBzM}]_0:[\text{DDT}]_0$) are provided.

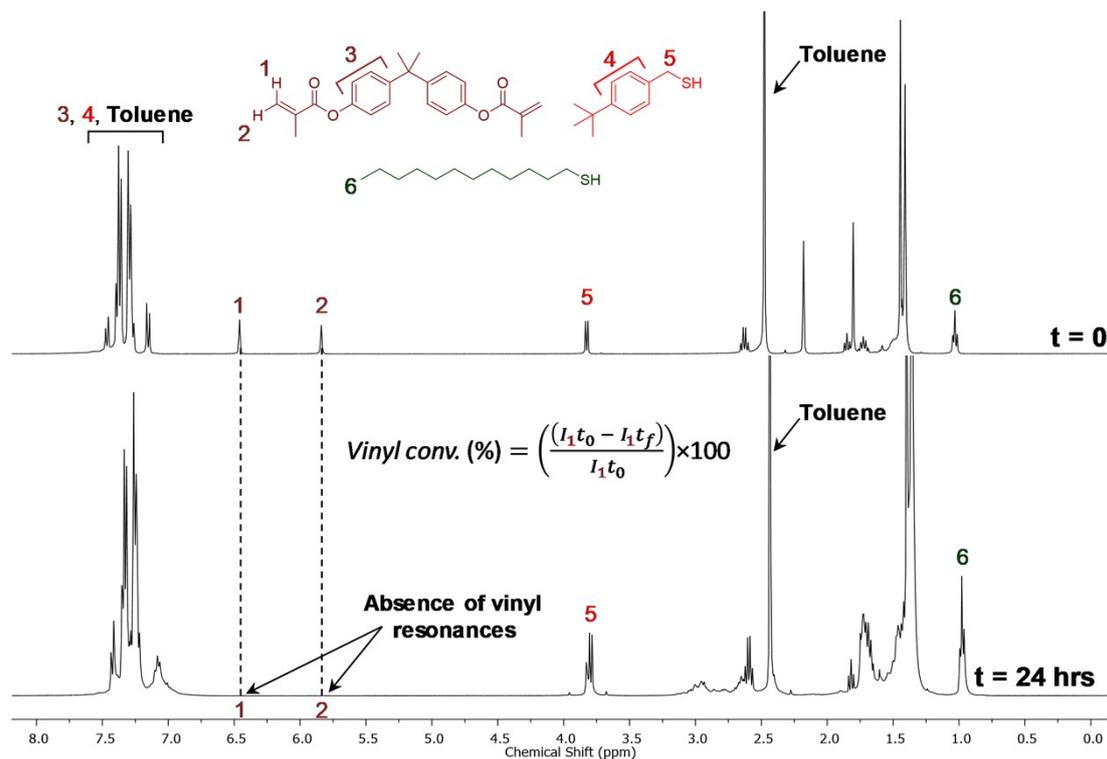


Figure S42 Overlaid ^1H NMR (400 MHz, CDCl_3) spectra obtained from the mixed telogen copolymerisation of DDT and *t*BuBzM with BPADMA prior to thermal initiation (top) and 24 hours after initiation (bottom). The equation provided was used to determine monomer conversion (integrals normalised with respect to 6).

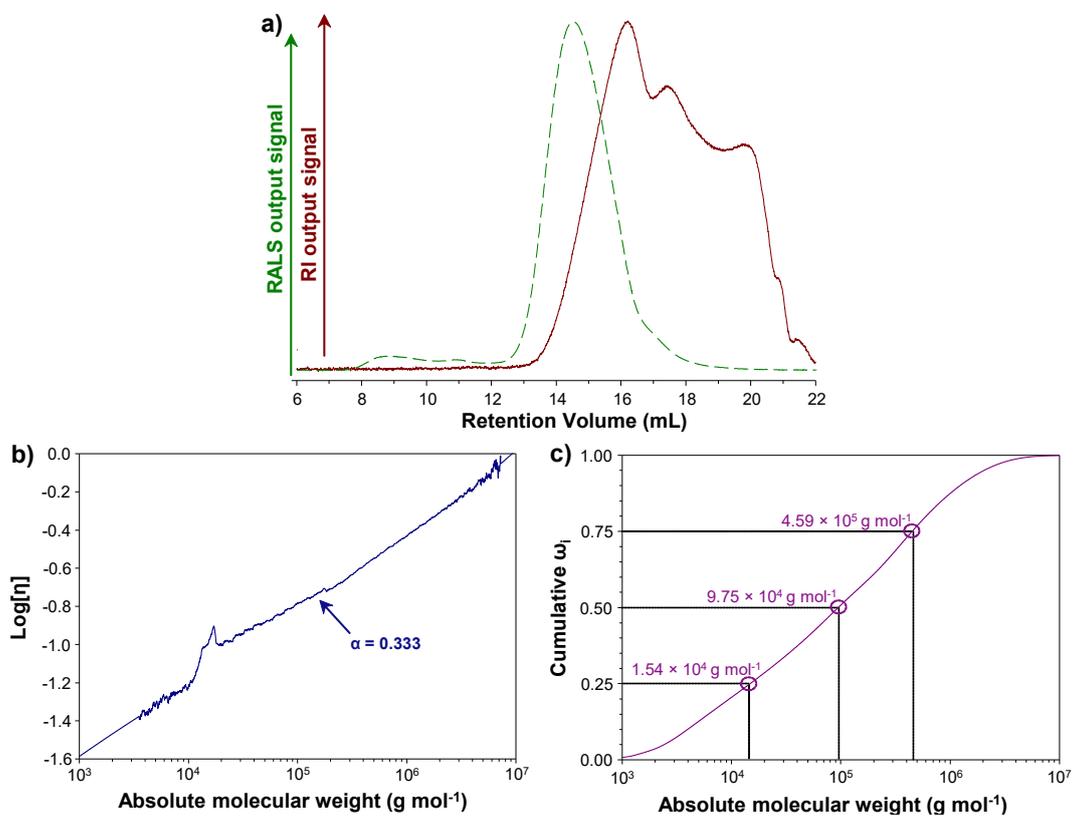


Figure S43 TD-SEC analysis of $p([t\text{BuBzM-BPADMA}]_{\text{stat}}\text{-[DDT-BPADMA]})$ a) Overlaid RI (red solid line) and RALS (green dashed line) chromatograms. b) Evaluation of copolymer topological structure *via* MHS analysis. c) Analysis of the relationship between absolute molecular weight and the cumulative weight fraction.

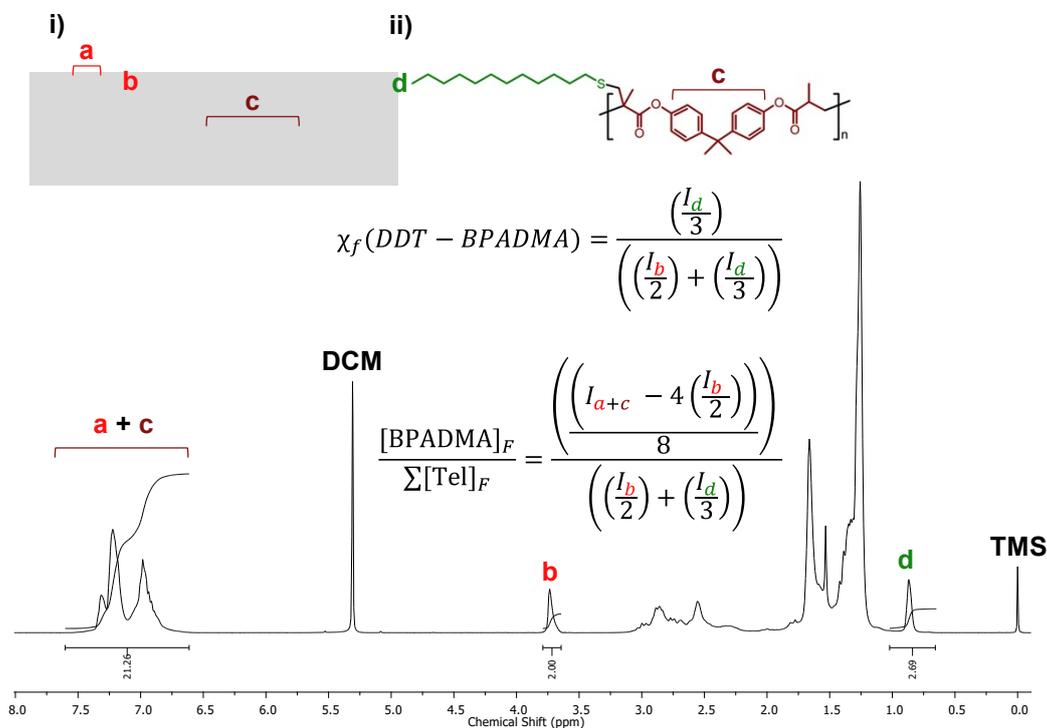


Figure S44 ^1H NMR spectrum (400 MHz, DCM-d_2) of $p([t\text{BuBzM-BPADMA}]_{\text{stat}}\text{-[DDT-BPADMA]})$ showing the calculations used to determine the final ratio of BPADMA to telogen ($[\text{BPADMA}]_F/\sum[\text{Tel}]_F$) and the telogen composition (mole fraction, χ_f) in the purified polymer.

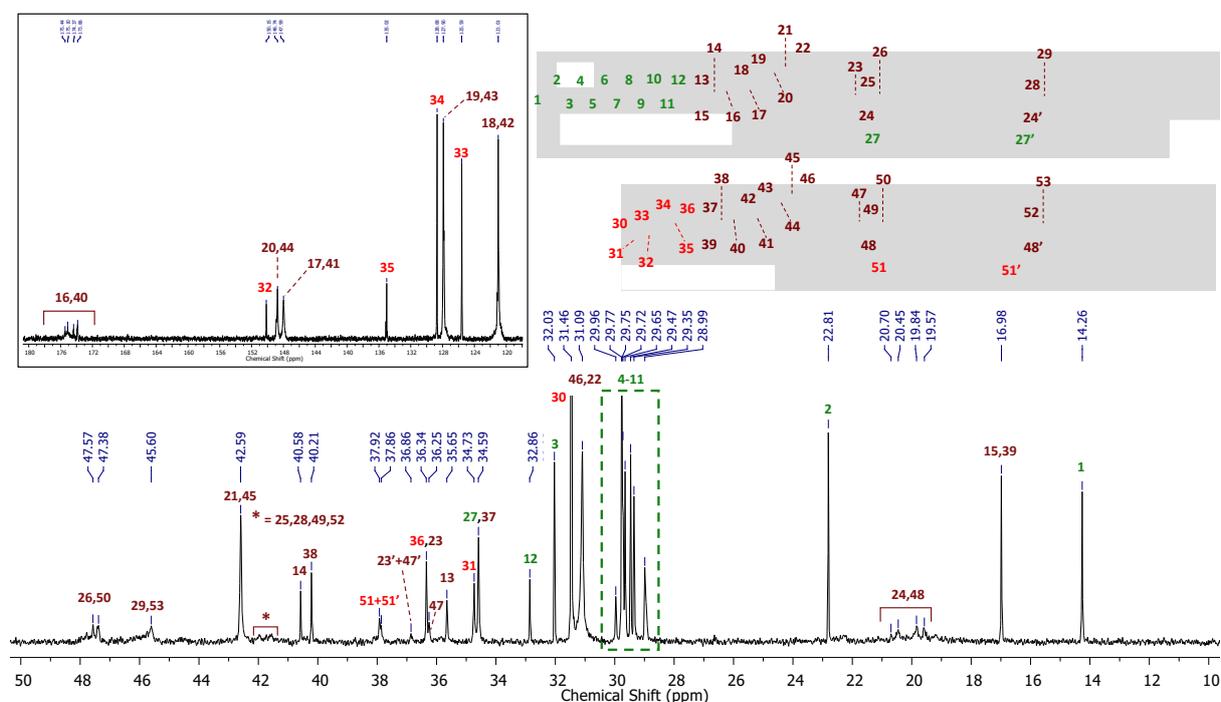


Figure S45 ^{13}C NMR (100 MHz, CDCl_3) spectrum of $p([t\text{BuBzM-BPADMA}]_{\text{stat}}\text{-[DDT-BPADMA]})$ including assignment of ^{13}C environments.

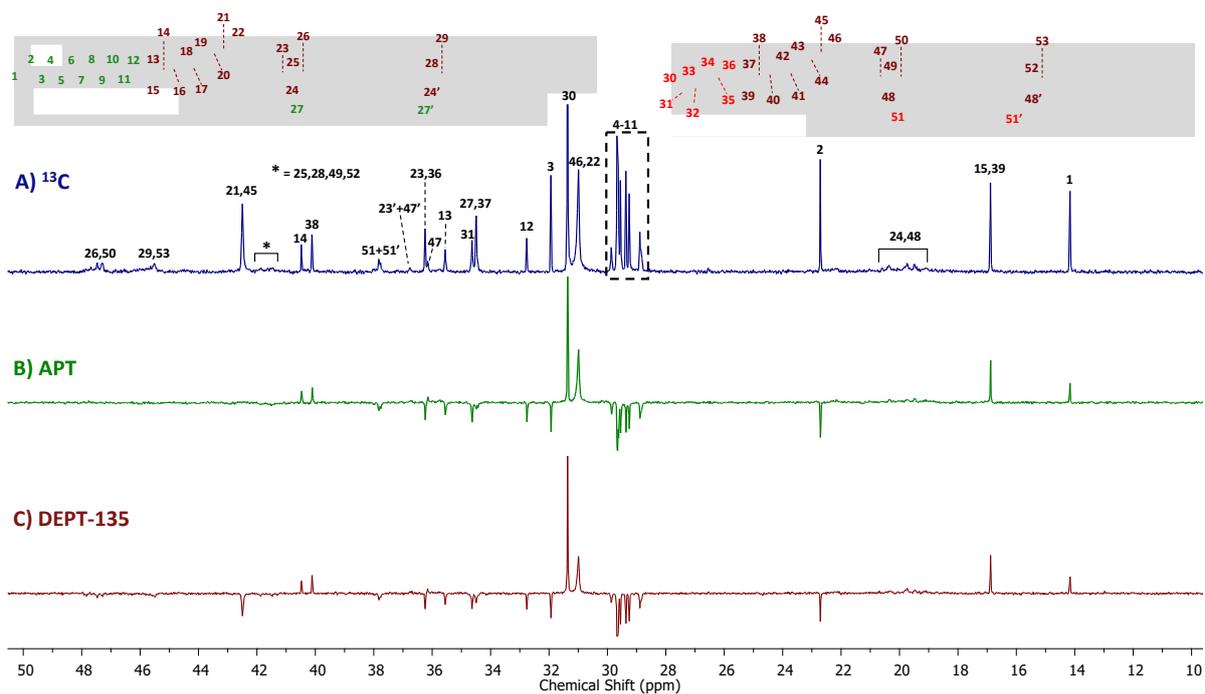


Figure S46 Overlaid A) ^{13}C , B) DEPT-135 and C) APT NMR (100 MHz, CDCl_3) spectra obtained from $p([t\text{BuBzM-BPADMA}]\text{-stat-}[\text{DDT-BPADMA}])$ including assignment of ^{13}C environments.

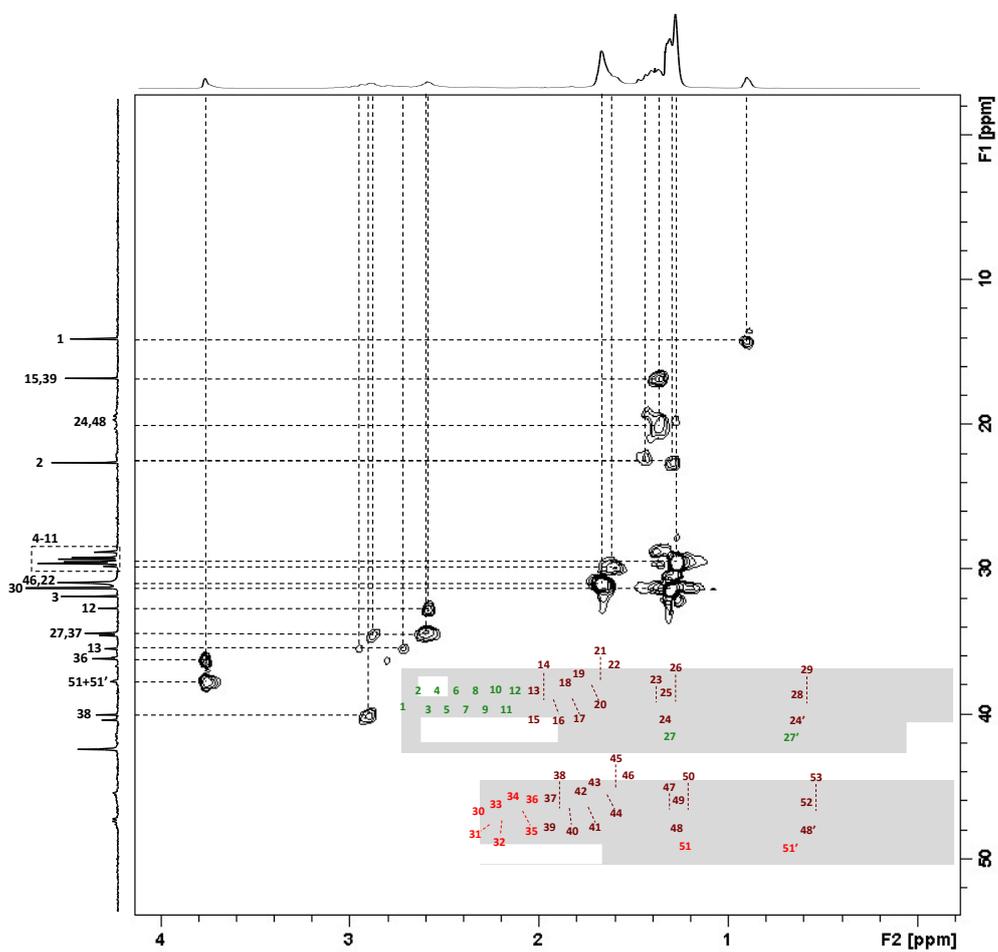


Figure S47 HSQC correlation of ^1H and ^{13}C NMR spectra obtained for $p([t\text{BuBzM-}i\text{BPADMA}]\text{-stat-}[\text{DDT-}i\text{BPADMA}])$, enabling assignment of several ^1H and ^{13}C environments.

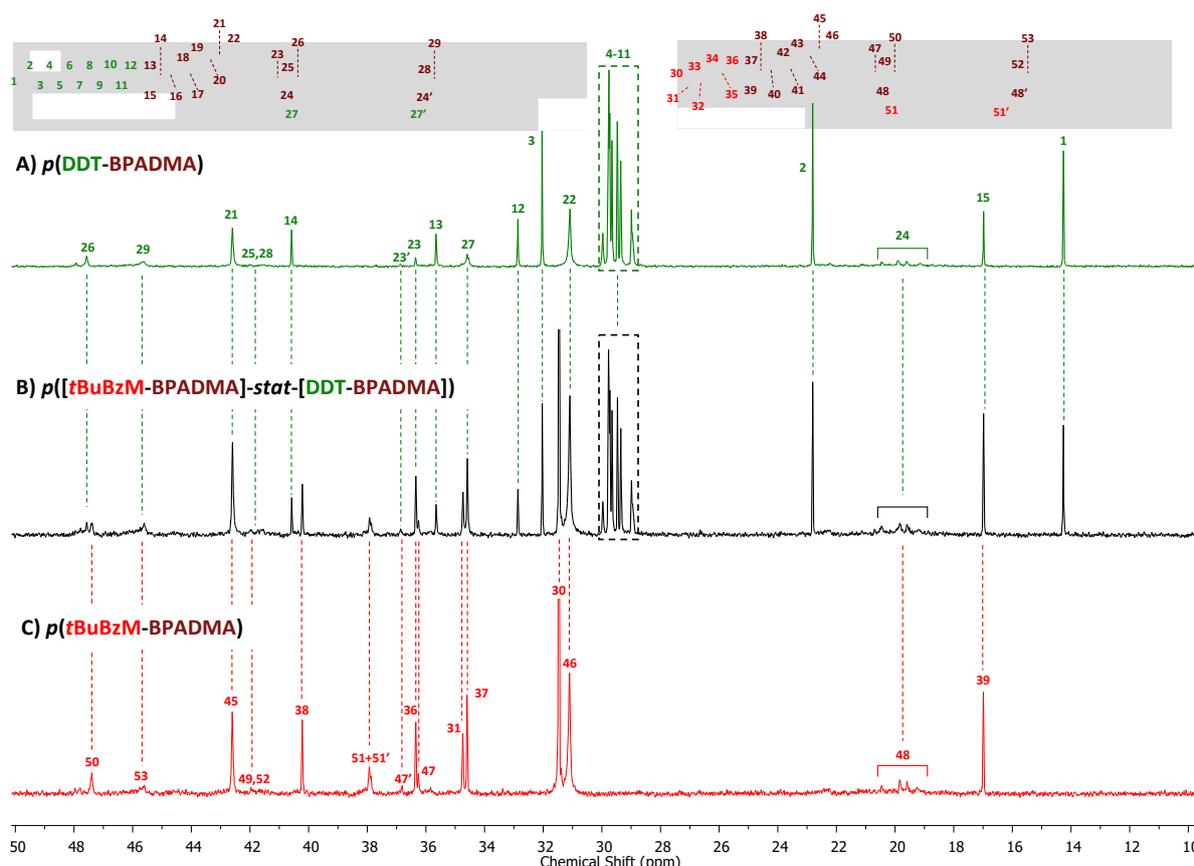


Figure S48 Overlaid ^{13}C NMR spectra (100 MHz, CDCl_3) obtained for A) $p(\text{DDT-}i\text{BPADMA})$, B) $p([t\text{BuBzM-}i\text{BPADMA}]\text{-stat-}[\text{DDT-}i\text{BPADMA}])$ and C) $p(t\text{BuBzM-}i\text{BPADMA})$. This shows the presence of key structural units from both $p(\text{DDT-}i\text{BPADMA})$ (green dashed lines) and $p(t\text{BuBzM-}i\text{BPADMA})$ (red dotted lines) repeat units, within the $p([t\text{BuBzM-}i\text{BPADMA}]\text{-stat-}[\text{DDT-}i\text{BPADMA}])$ NMR spectrum.

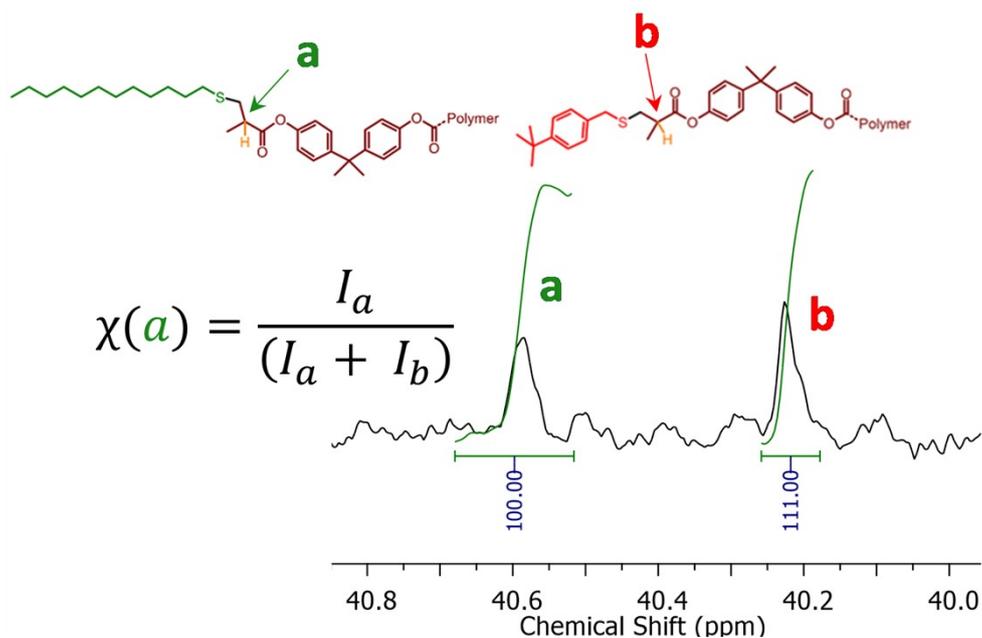


Figure S49 Inverse-gated ^{13}C NMR spectra (100 MHz, CDCl_3) obtained $p([t\text{BuBzM-}i\text{BPADMA}]\text{-stat-}[\text{DDT-}i\text{BPADMA}])$, showing the relative intensities of key structural units within the branched copolymer structure.

2.2.7 Synthesis & characterisation of *p*([DDT-BPADMA]-*stat*-[DDT-EGDMA])

BPADMA (3.00 g, 8.23 mmol, 0.250 equiv.), EGDMA (1.63 g, 8.23 mmol, 0.250 equiv.) DDT (6.66 g, 32.9 mmol, 1.000 equiv.) and AIBN (0.081 g, 0.494 mmol) were placed into a 25 mL round-bottom flask. Toluene (50 wt % based on BPADMA, EGDMA and DDT; 11.38 g, 13.13 mL) was added and the solution was deoxygenated using a nitrogen purge under magnetic stirring for 30 minutes. An aliquot (~100 μ L) of the mixture was taken for determination of the initial molar ratios of: (i) total MVT to telogen ($\Sigma[\text{MVT}]_0/[\text{Tel}]_0$) and (ii) the composition of the MVT mixture ($[\text{BPADMA}]_0/\Sigma[\text{MVT}]_0$) by ^1H NMR analysis (Figure S50). The flask was then placed in an oil bath at 100 $^\circ\text{C}$ for 24 hours. The reaction was stopped *via* cooling and exposure to air. An aliquot (~100 μ L) of the reaction mixture was taken for determination of monomer conversion *via* ^1H NMR (Figure S51). The reaction mixture was then diluted in THF and precipitated into methanol twice (using a good solvent: anti-solvent volume ratio of 1:20) at ambient temperature, yielding a white precipitate. The polymer was dried *in vacuo* at 40 $^\circ\text{C}$ overnight to yield *p*([DDT-BPADMA]-*stat*-[DDT-EGDMA]) as a white powder. The product was analysed by TD-SEC (Figure S52) and several ^1H and ^{13}C NMR spectroscopic techniques (Figure S53-S58).

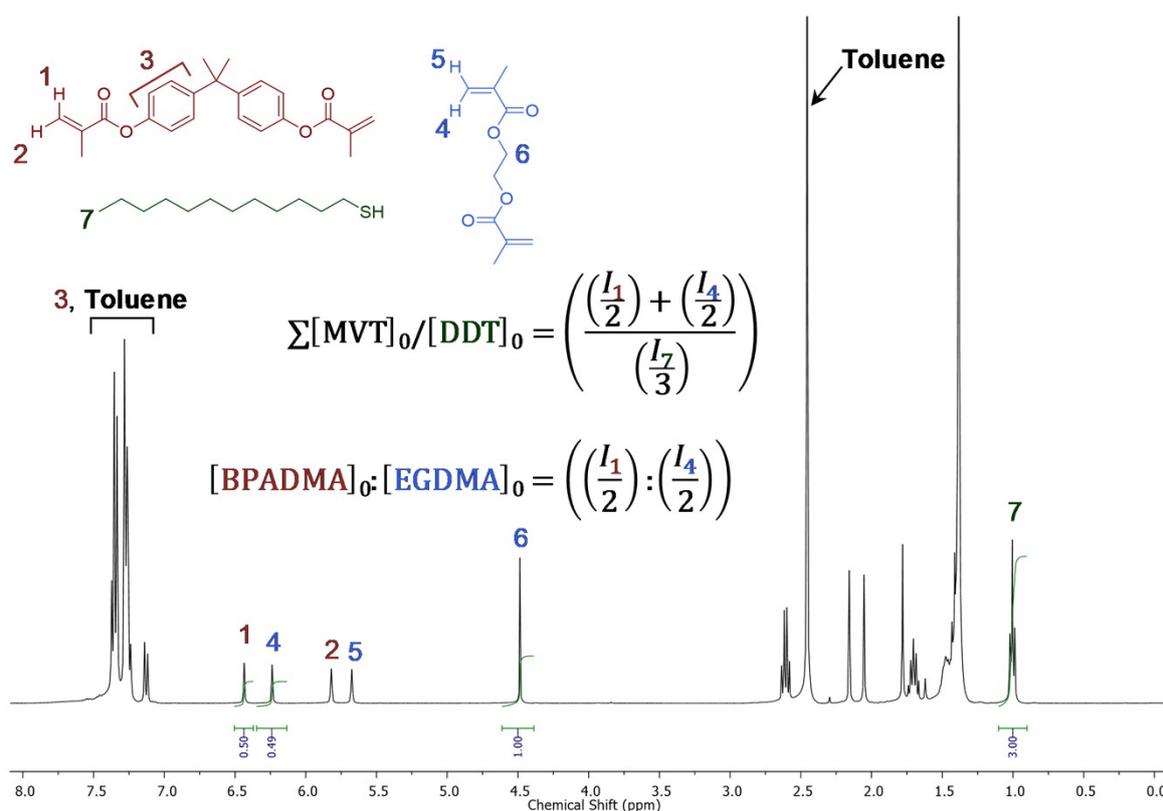


Figure S50 ^1H NMR (400 MHz, CDCl_3) spectrum obtained from the mixed multi-vinyl taxogen (MVT) copolymerisation of BPADMA and EGDMA with DDT, prior to thermal initiation ($t = 0$). The equations used to determine the initial ratio of MVT to DDT ($\Sigma[\text{MVT}]_0/[\text{DDT}]_0$) and the composition of the MVT mixture ($[\text{BPADMA}]_0:[\text{EGDMA}]_0$) are provided.

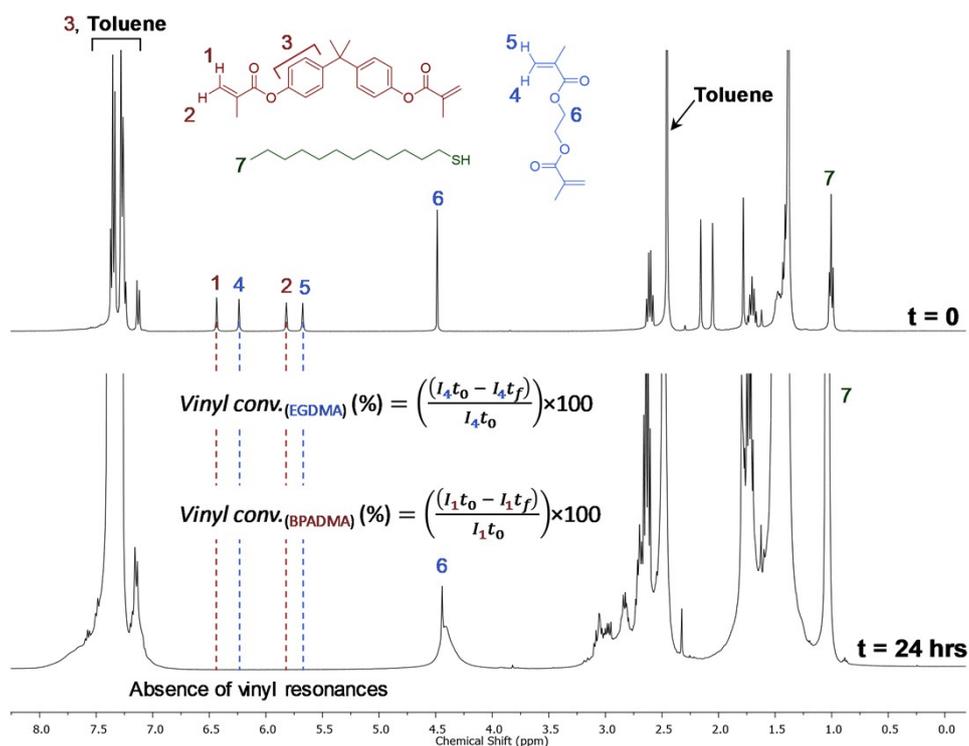


Figure S51 Overlaid ^1H NMR (400 MHz, CDCl_3) spectra obtained from the mixed MVT copolymerisation of BPADMA and EGDMA with DDT, prior to thermal initiation (top) and 24 hours after initiation (bottom). The equation provided was used to determine monomer conversion (integrals normalised with respect to 7).

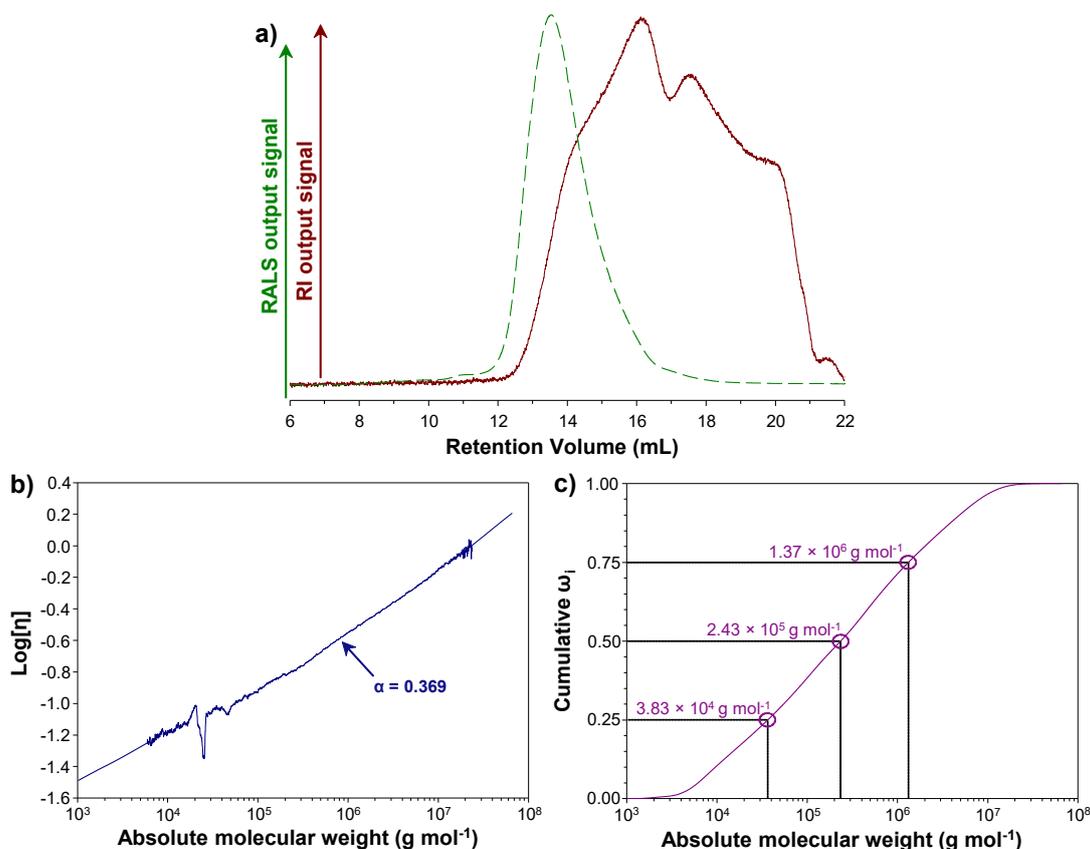


Figure S52 TD-SEC analysis of p ([DDT-BPADMA]-*stat*-[DDT-EGDMA]). a) Overlaid RI (red solid line) and RALS (green dashed line) chromatograms. b) Evaluation of copolymer topological structure *via* MHS analysis. c) Analysis of the relationship between absolute molecular weight and the cumulative weight fraction.

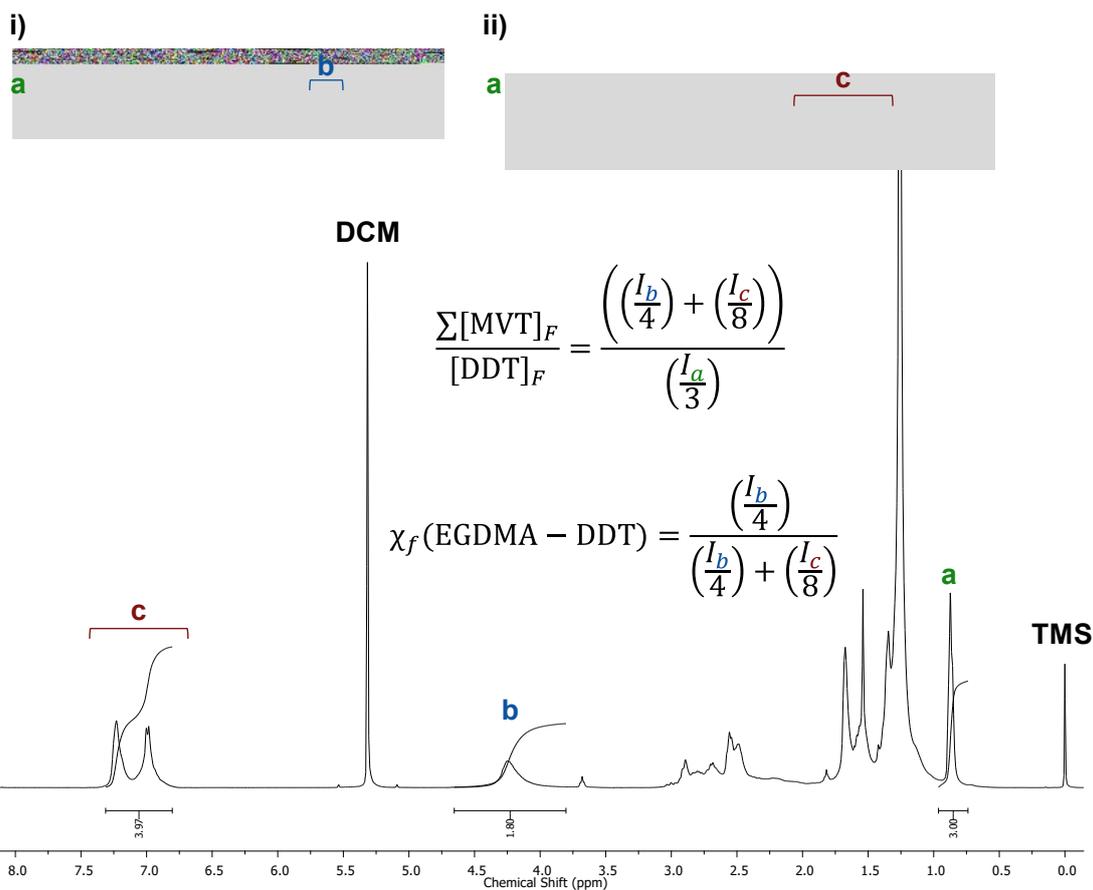


Figure S53 ^1H NMR spectrum (400 MHz, DCM-d_2) of $p([\text{DDT-BPADMA}]\text{-stat-}[\text{DDT-EGDMA}])$ showing the calculations used to determine the final ratio of MVT to DDT ($\frac{\sum[\text{MVT}]_F}{[\text{DDT}]_F}$) and MVT compositions (mole fractions, χ_f) in the purified polymer.

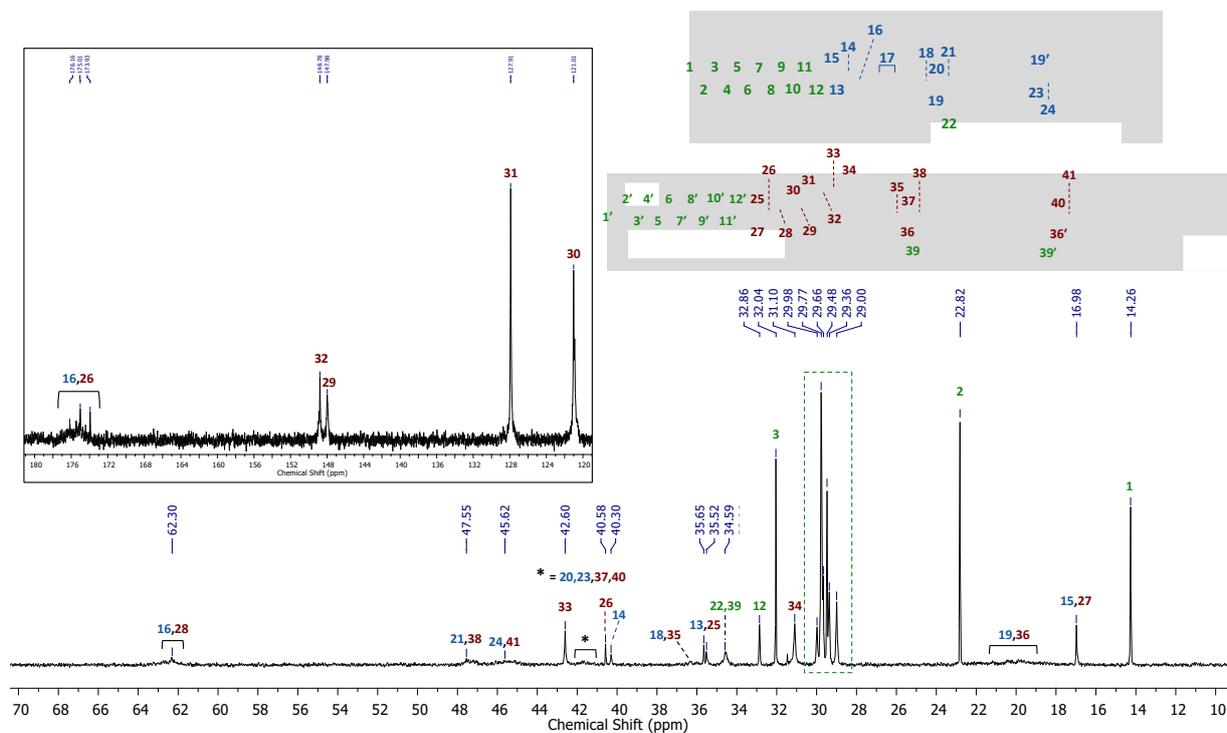


Figure S54 ^{13}C NMR (100 MHz, CDCl_3) spectrum of $p([\text{DDT-BPADMA}]\text{-stat-}[\text{DDT-EGDMA}])$ including assignment of ^{13}C environments.

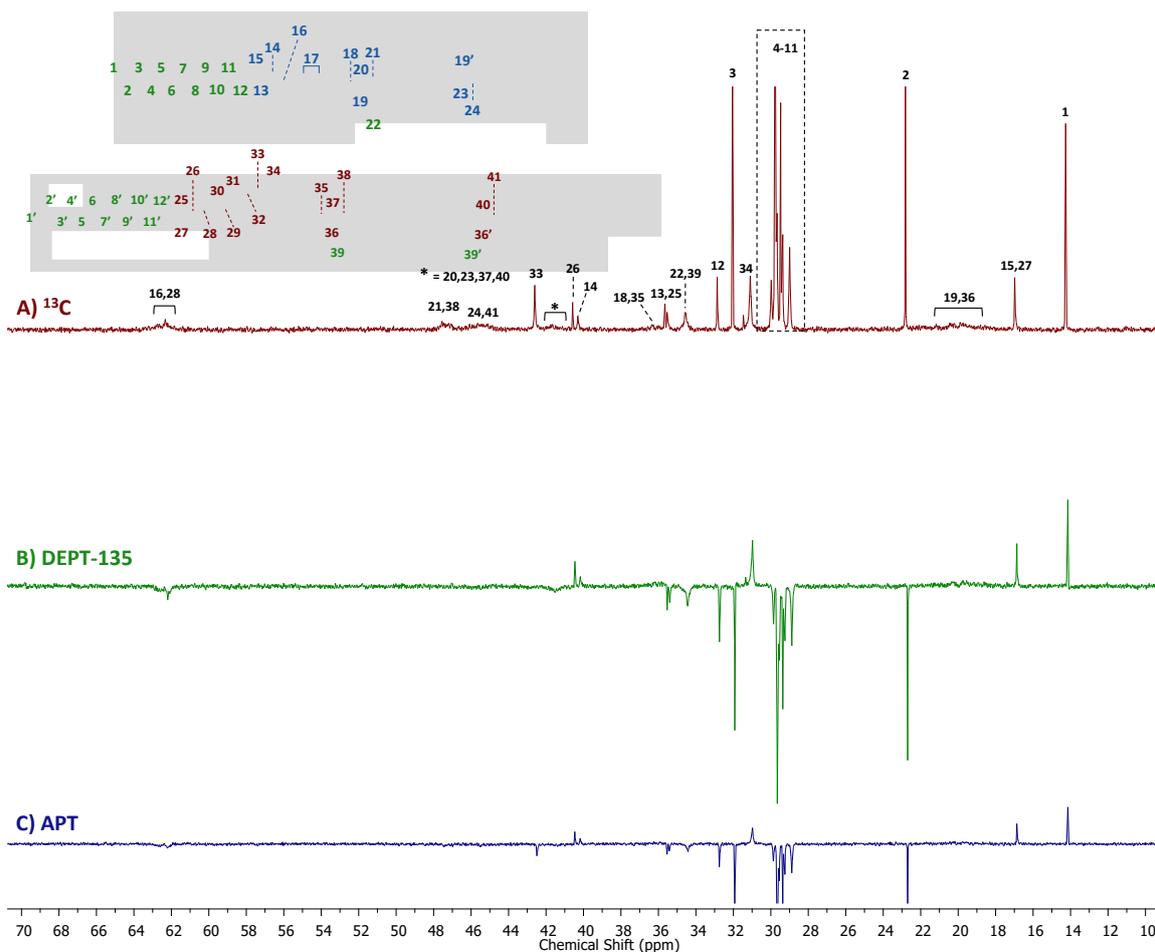


Figure S55 Overlaid A) ^{13}C , B) DEPT-135 and C) APT NMR (100 MHz, CDCl_3) spectra obtained from $p[(\text{DDT-BPADMA})\text{-stat}-(\text{DDT-EGDMA})]$ including assignment of ^{13}C environments.

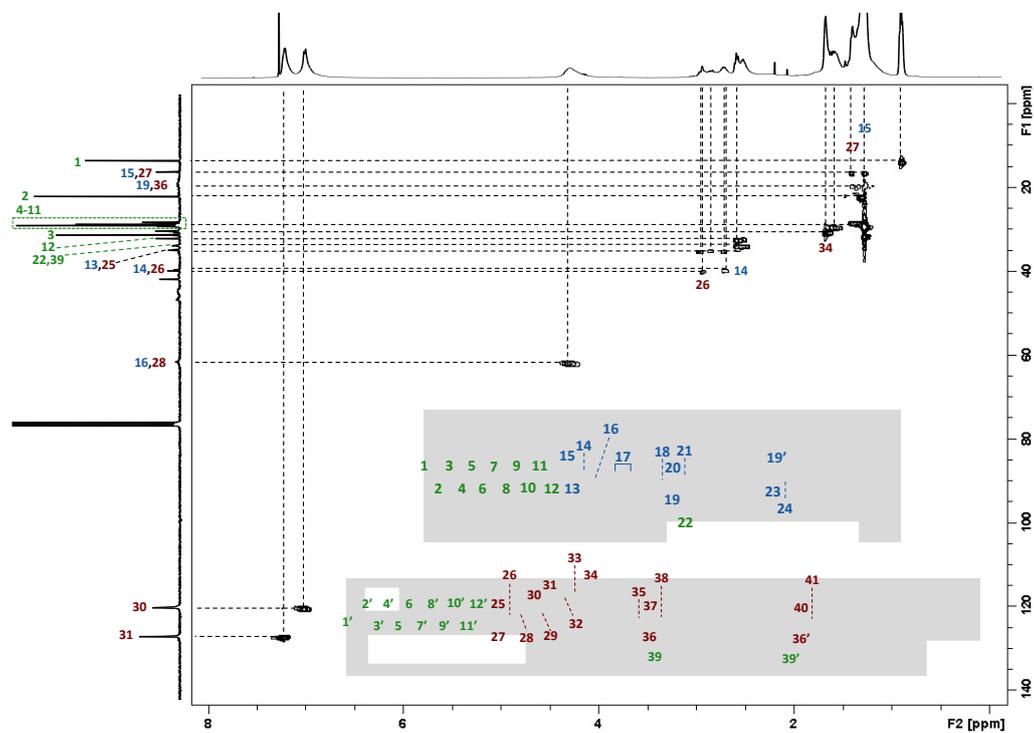


Figure S56 HSQC correlation of ^1H and ^{13}C NMR spectra obtained $p[(\text{DDT-BPADMA})\text{-stat}-(\text{DDT-EGDMA})]$, enabling assignment of several ^1H and ^{13}C environments.

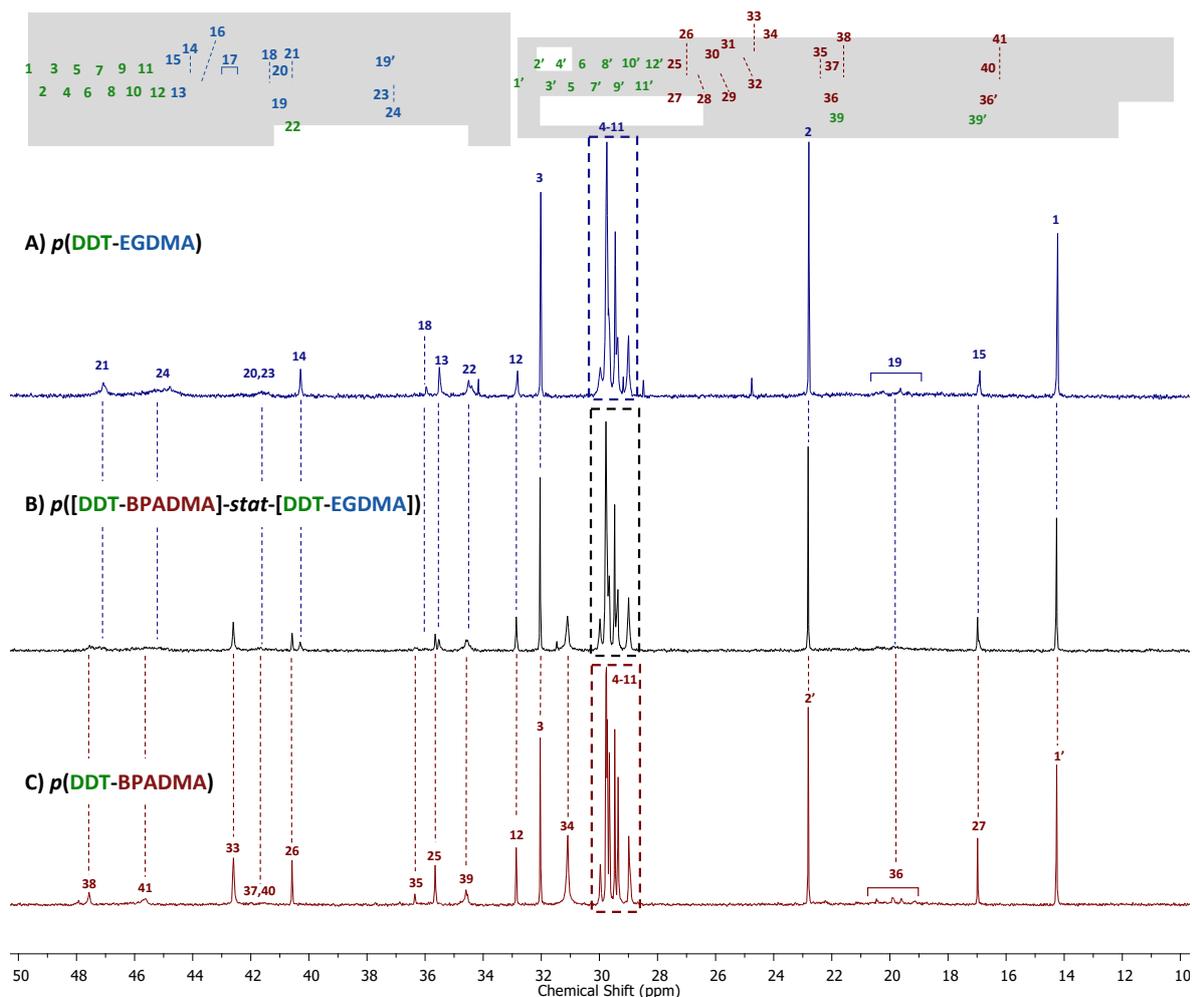


Figure S57 Overlaid ^{13}C NMR spectra (100 MHz, CDCl_3) obtained for A) $p(\text{DDT-BPADMA})$, B) $p([\text{DDT-BPADMA}]\text{-stat-}[\text{DDT-EGDMA}])$ and C) $p(\text{DDT-EGDMA})$. This shows the presence of key structural units from both $p(\text{DDT-BPADMA})$ (dark red dashed lines) and $p(\text{DDT-EGDMA})$ (blue dotted lines) repeat units, within the $p([\text{DDT-BPADMA}]\text{-stat-}[\text{DDT-EGDMA}])$ NMR spectrum.

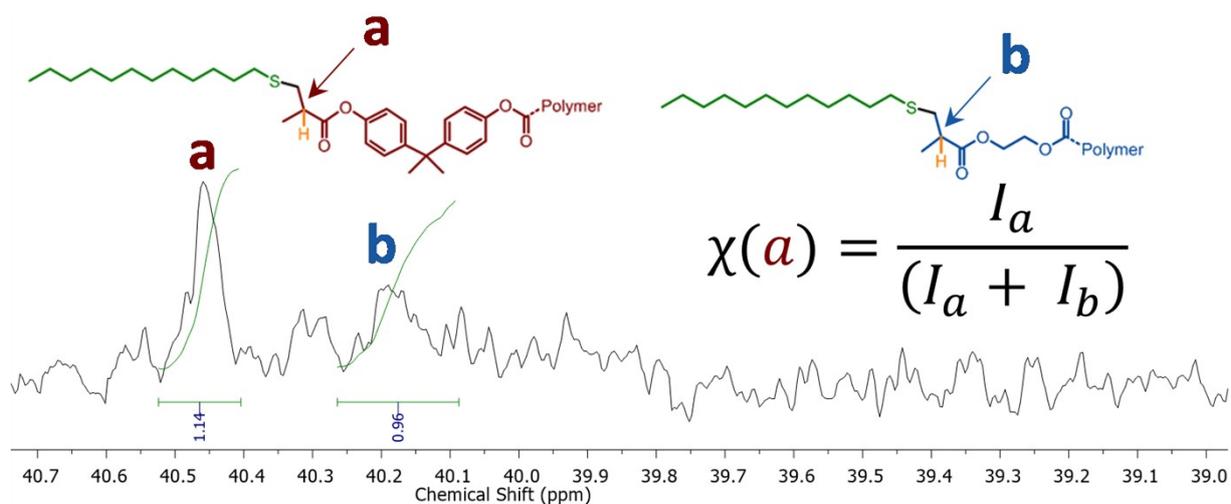


Figure S58 Inverse-gated ^{13}C NMR spectra (100 MHz, CDCl_3) obtained from $p([\text{DDT-BPADMA}]\text{-stat-}[\text{DDT-EGDMA}])$, showing the relative intensities of key structural units within the branched copolymer structure.

2.2.8 Synthesis & characterisation of $p([t\text{BuBzM-BPADMA}]\text{-stat-}[t\text{BuBzM-EGDMA}])$

BPADMA (0.919 g, 2.52 mmol, 0.275 equiv.), EGDMA (0.500 g, 2.52 mmol, 0.275 equiv.) $t\text{BuBzM}$ (1.65 g, 9.17 mmol, 1.000 equiv.) and AIBN (0.025 g, 0.151 mmol) were placed into a 25 mL round-bottom flask. Toluene (50 wt % based on BPADMA, EGDMA and DDT; 3.10 g, 3.58 mL) was added and the solution was deoxygenated using a nitrogen purge under magnetic stirring for 30 minutes. An aliquot ($\sim 100\ \mu\text{L}$) of the mixture was taken for determination of the initial molar ratios of: (i) total MVT to telogen ($\sum[\text{MVT}]_0/[\text{Tel}]_0$) and (ii) the composition of the MVT mixture ($[\text{BPADMA}]_0/\sum[\text{MVT}]_0$) by ^1H NMR analysis (Figure S60). The flask was then placed in an oil bath at $100\ ^\circ\text{C}$ for 24 hours. The reaction was stopped *via* cooling and exposure to air. An aliquot ($\sim 100\ \mu\text{L}$) of the reaction mixture was taken for determination of monomer conversion *via* ^1H NMR (Figure S61). The reaction mixture was then diluted in THF and precipitated into methanol twice (using a good solvent: anti-solvent volume ratio of 1:20) at ambient temperature, yielding a white precipitate. The polymer was dried *in vacuo* at $40\ ^\circ\text{C}$ overnight to yield $p([t\text{BuBzM-BPADMA}]\text{-stat-}[t\text{BuBzM-EGDMA}])$ as a white powder. The product was analysed by TD-SEC (Figure S59) and several ^1H and ^{13}C NMR spectroscopic techniques (Figure S63-S67).

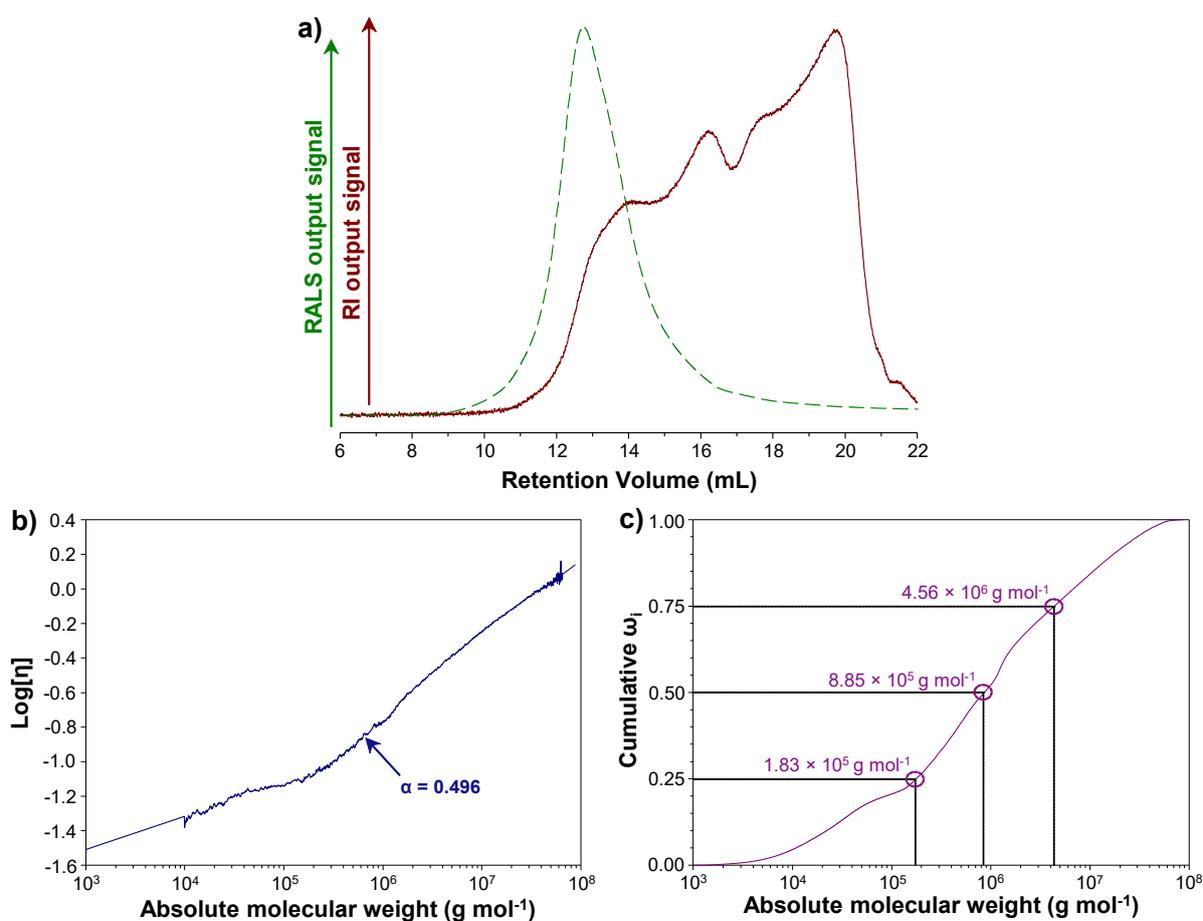


Figure S59 TD-SEC analysis of $p([t\text{BuBzM-BPADMA}]\text{-stat-}[t\text{BuBzM-EGDMA}])$. a) Overlaid RI (red solid line) and RALS (green dashed line) chromatograms. b) Evaluation of copolymer topological structure *via* MHS analysis. c) Analysis of the relationship between absolute molecular weight and the cumulative weight fraction.

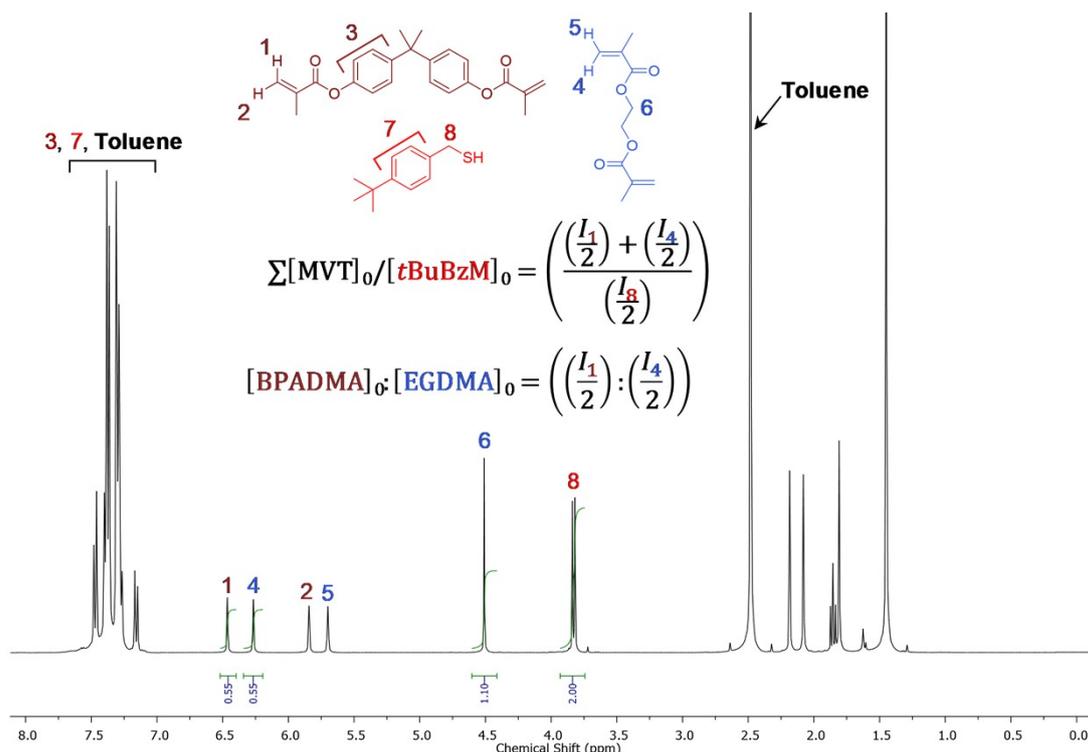


Figure S60 ^1H NMR (400 MHz, CDCl_3) spectrum obtained from the mixed MVT copolymerisation of BPADMA and EGDMA with *t*BuBzM, prior to thermal initiation ($t = 0$). The equations used to determine the initial ratio of MVT to *t*BuBzM ($\sum[MVT]_0/[tBuBzM]_0$) and the composition of the MVT mixture ($[BPADMA]_0:[EGDMA]_0$) are provided.

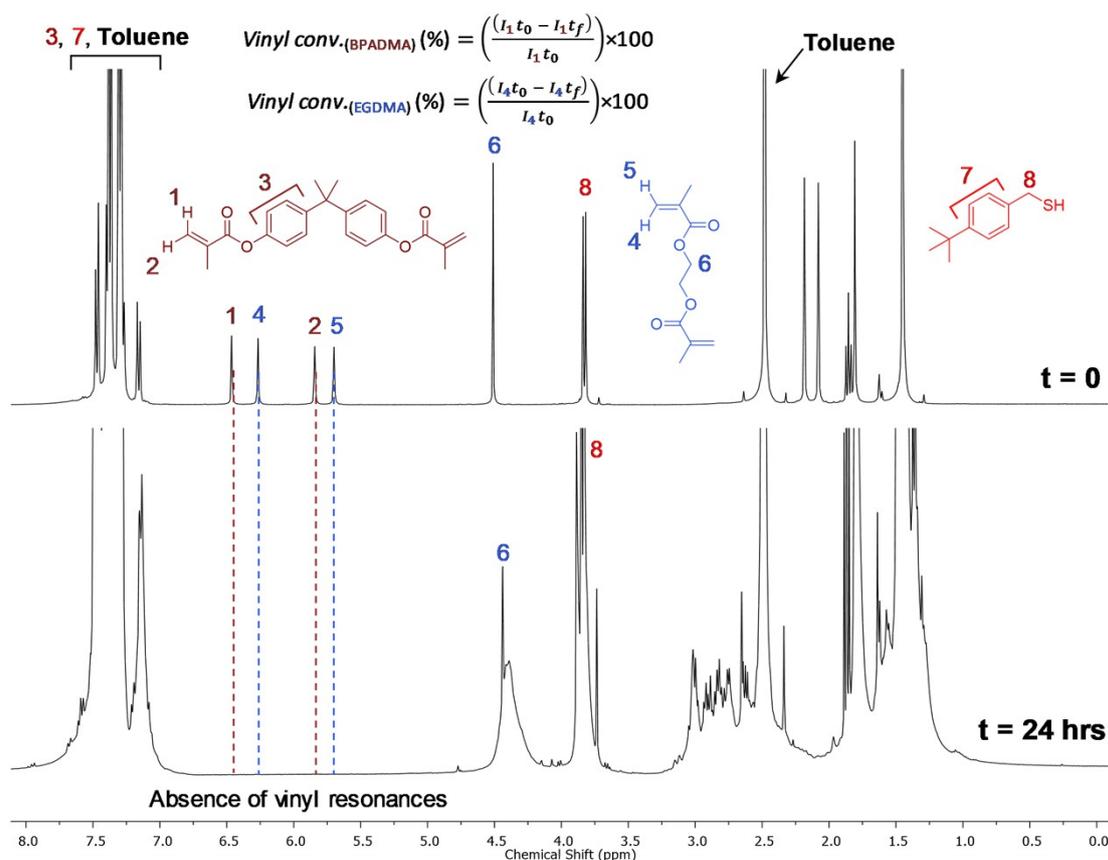


Figure S61 Overlaid ^1H NMR (400 MHz, CDCl_3) spectra obtained from the mixed MVT copolymerisation of BPADMA and EGDMA with *t*BuBzM, prior to thermal initiation (top) and 24 hours after initiation (bottom). The equation provided was used to determine monomer conversion (integrals normalised with respect to 8).

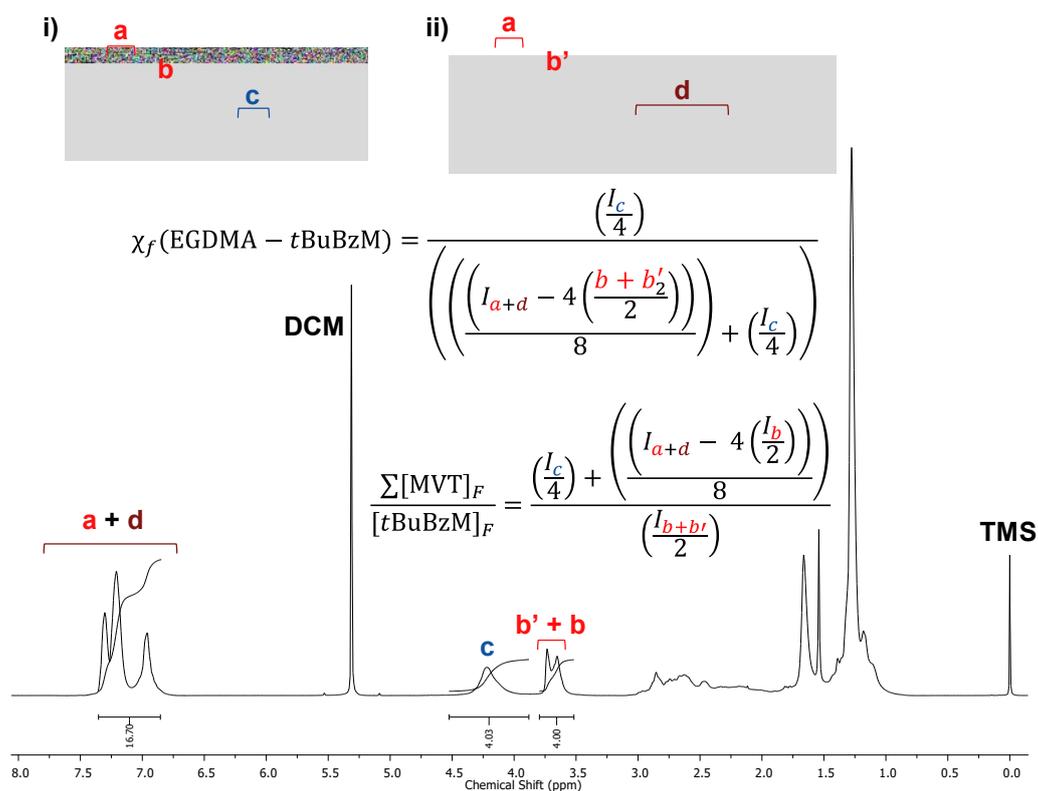


Figure S62 ^1H NMR spectrum (400 MHz, DCM-d_2) of $p([t\text{BuBzM-BPADMA}]\text{-stat-}[t\text{BuBzM-EGDMA}])$ showing the calculations used to determine the final ratio of MVT to $t\text{BuBzM}$ ($\sum[\text{MVT}]_F/[t\text{BuBzM}]_F$) and MVT compositions (mole fractions, χ_f) in the purified polymer.

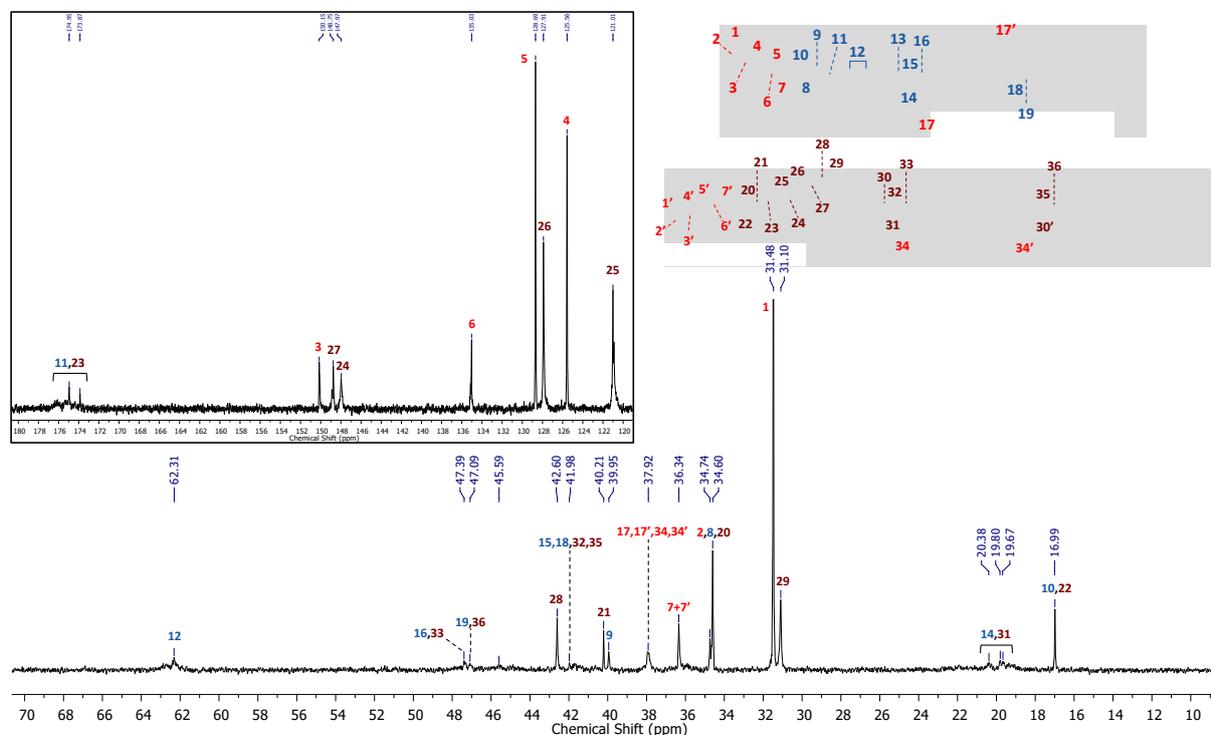


Figure S63 ^{13}C NMR (100 MHz, CDCl_3) spectrum of $p([t\text{BuBzM-BPADMA}]\text{-stat-}[t\text{BuBzM-EGDMA}])$ including assignment of ^{13}C environments.

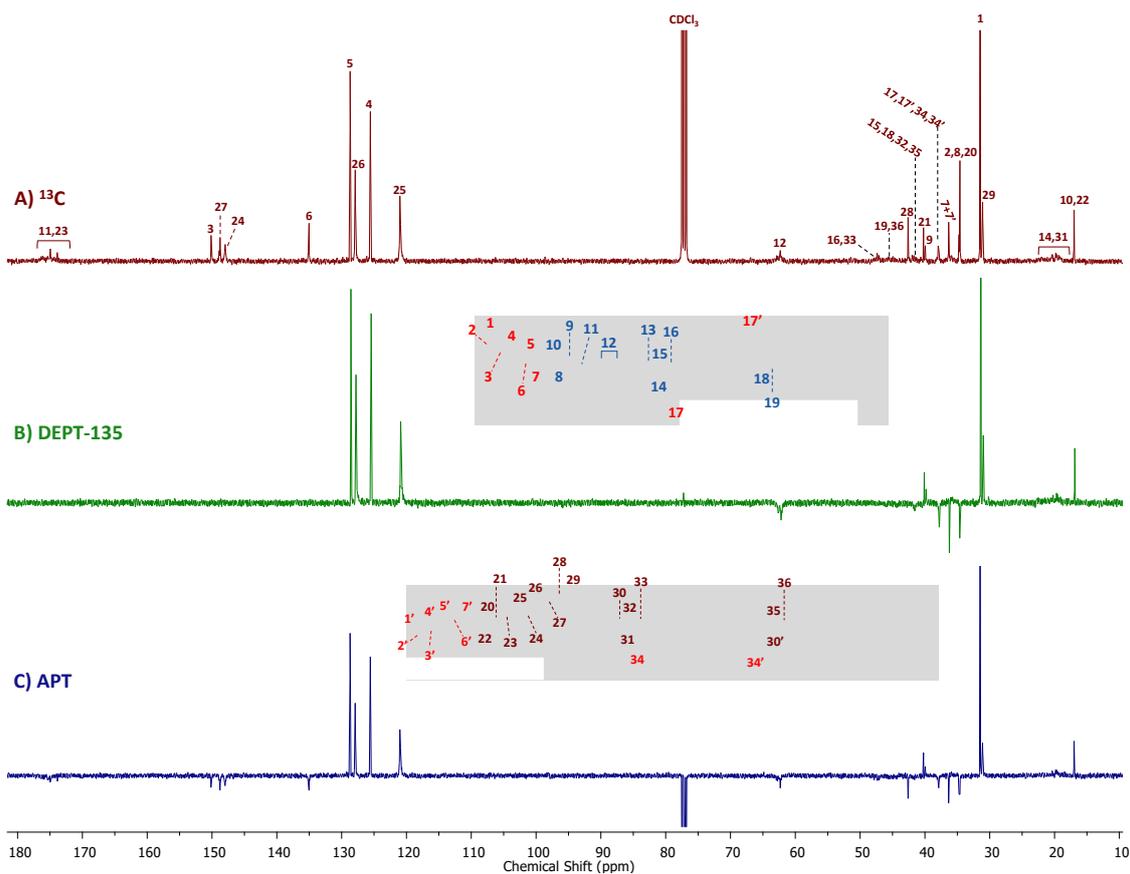


Figure S64 Overlaid A) ^{13}C , B) DEPT-135 and C) APT NMR (100 MHz, CDCl_3) spectra obtained from $p([t\text{BuBzM-BPADMA}]\text{-stat-}[t\text{BuBzM-EGDMA}])$ including assignment of ^{13}C environments.

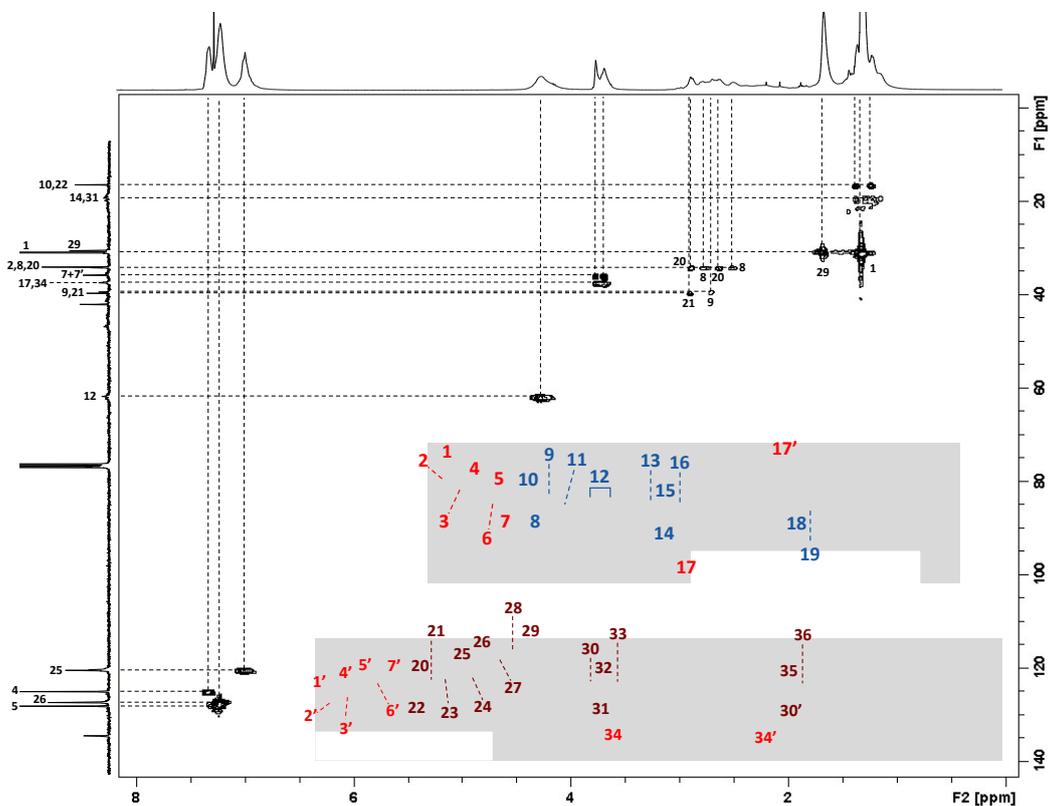


Figure S65 HSQC correlation of ^1H and ^{13}C NMR spectra obtained from $p([t\text{BuBzM-BPADMA}]\text{-stat-}[t\text{BuBzM-EGDMA}])$, enabling assignment of several ^1H and ^{13}C environments.

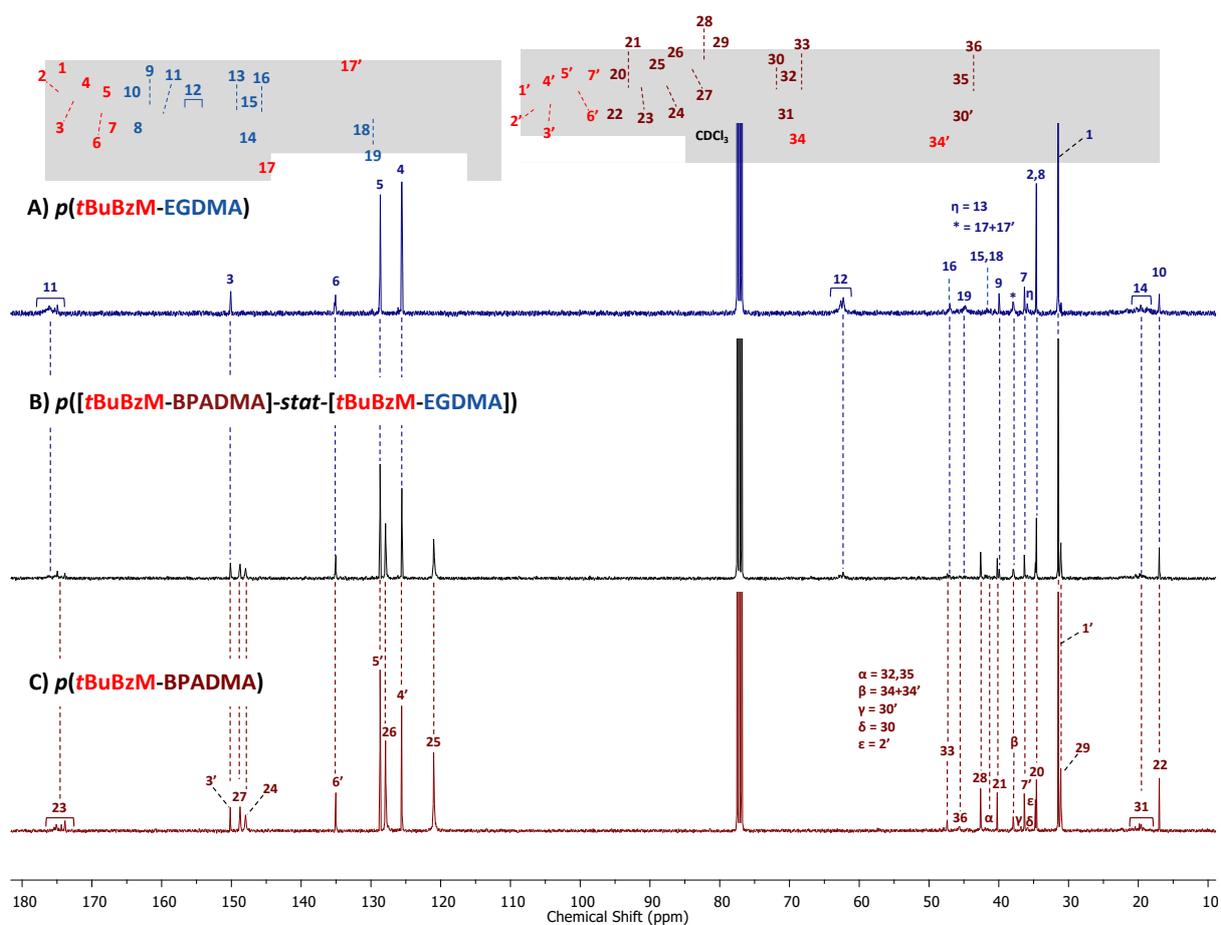


Figure S66 Overlaid ^{13}C NMR spectra (100 MHz, CDCl_3) obtained for A) $p(t\text{BuBzM-BPADMA})$, B) $p([t\text{BuBzM-BPADMA}]\text{-stat-[}t\text{BuBzM-EGDMA}])$ and C) $p(t\text{BuBzM-EGDMA})$. This shows the presence of key structural units from both $p(t\text{BuBzM-BPADMA})$ (dark red dashed lines) and $p(t\text{BuBzM-EGDMA})$ (blue dotted lines) repeat units, within the $p([\text{DDT-BPADMA}]\text{-stat-[DDT-EGDMA}])$ NMR spectrum.

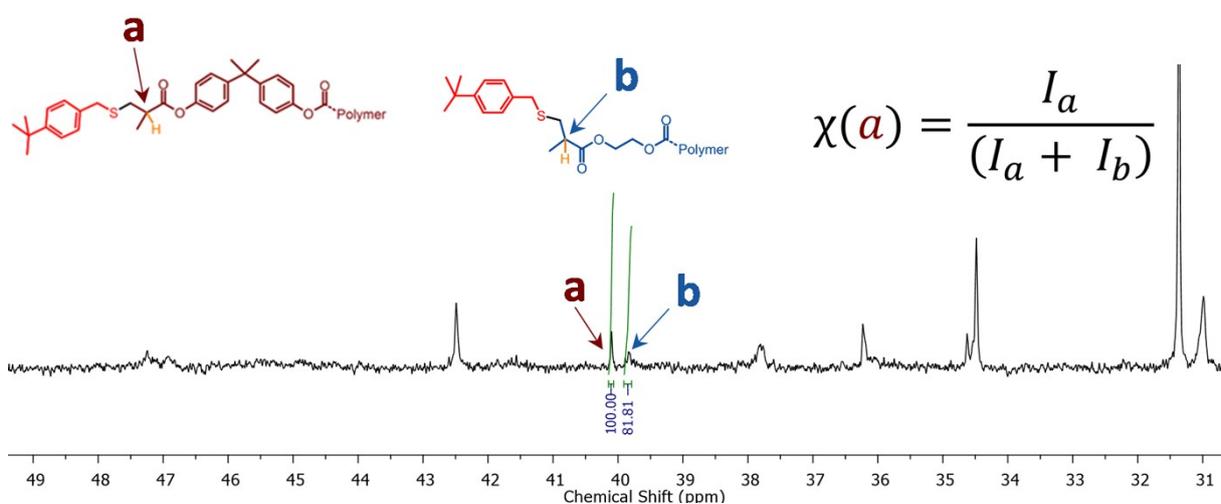


Figure S67 Inverse-gated ^{13}C NMR spectra (100 MHz, CDCl_3) obtained for $p([t\text{BuBzM-BPADMA}]\text{-stat-[}t\text{BuBzM-EGDMA}])$, showing the relative intensities of key structural units within the branched copolymer structure.

2.2.9 Synthesis & characterisation of *p*([DDT-EGDMA]-*stat*-BzMA)

EGDMA (3.00 g, 15.1 mmol, 0.925 equiv.), BzMA (2.67 g, 15.1 mmol, 0.925 equiv.), DDT (3.30 g, 16.3 mmol, 1.000 equiv.) and AIBN (0.112 g, 0.680 mmol) were placed into a 25 mL round-bottom flask. Ethyl acetate (50 wt % based on EGDMA, BzMA and DDT; 9.08 g, 10.07 mL) was added and the solution was deoxygenated using a nitrogen purge under magnetic stirring for 30 minutes. An aliquot (~100 μ L) of the mixture was taken for determination of the initial molar ratios of: (i) EGDMA to DDT ($[EGDMA]_0/[DDT]_0$) and (ii) EGDMA to BzMA ($[EGDMA]_0:[BzMA]_0$) by ^1H NMR analysis (Figure S69). The flask was then placed in an oil bath at 70 $^\circ\text{C}$ for 24 hours. The reaction was stopped *via* cooling and exposure to air. An aliquot (~100 μ L) of the reaction mixture was taken for determination of monomer conversion *via* ^1H NMR (Figure S70). The reaction mixture was then diluted in THF and precipitated into methanol twice (using a good solvent: anti-solvent volume ratio of 1:20) at ambient temperature, yielding a white precipitate. The polymer was dried *in vacuo* at 40 $^\circ\text{C}$ overnight to yield *p*([DDT-EGDMA]-*stat*-BzMA) as a white powder. The product was analysed by TD-SEC (Figure S68) and several ^1H and ^{13}C NMR spectroscopic techniques (Figure S71-S75).

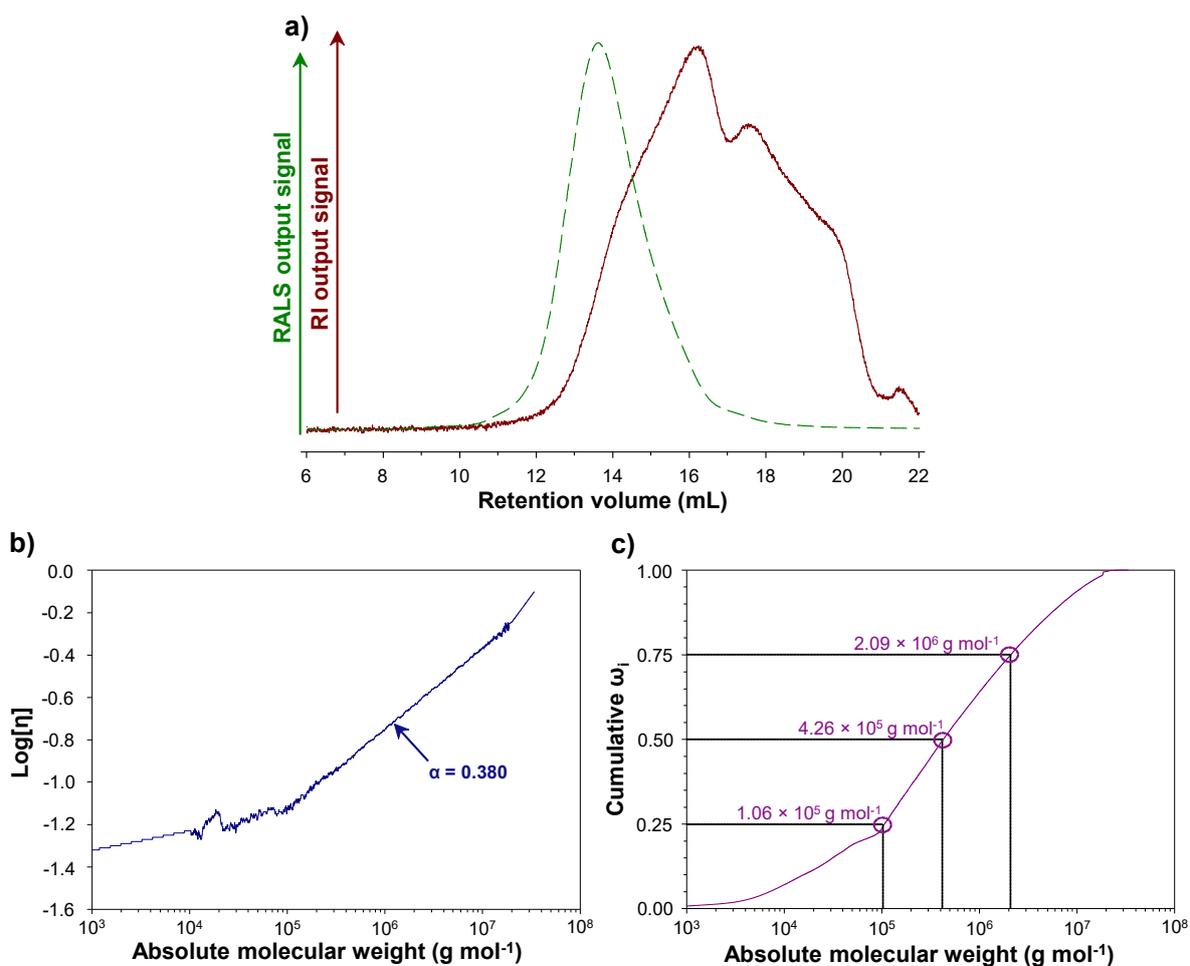


Figure S68 TD-SEC analysis of *p*([DDT-EGDMA]-*stat*-BzMA). a) Overlaid RI (red solid line) and RALS (green dashed line) chromatograms. b) Evaluation of copolymer topological structure *via* MHS analysis. c) Analysis of the relationship between absolute molecular weight and the cumulative weight fraction.

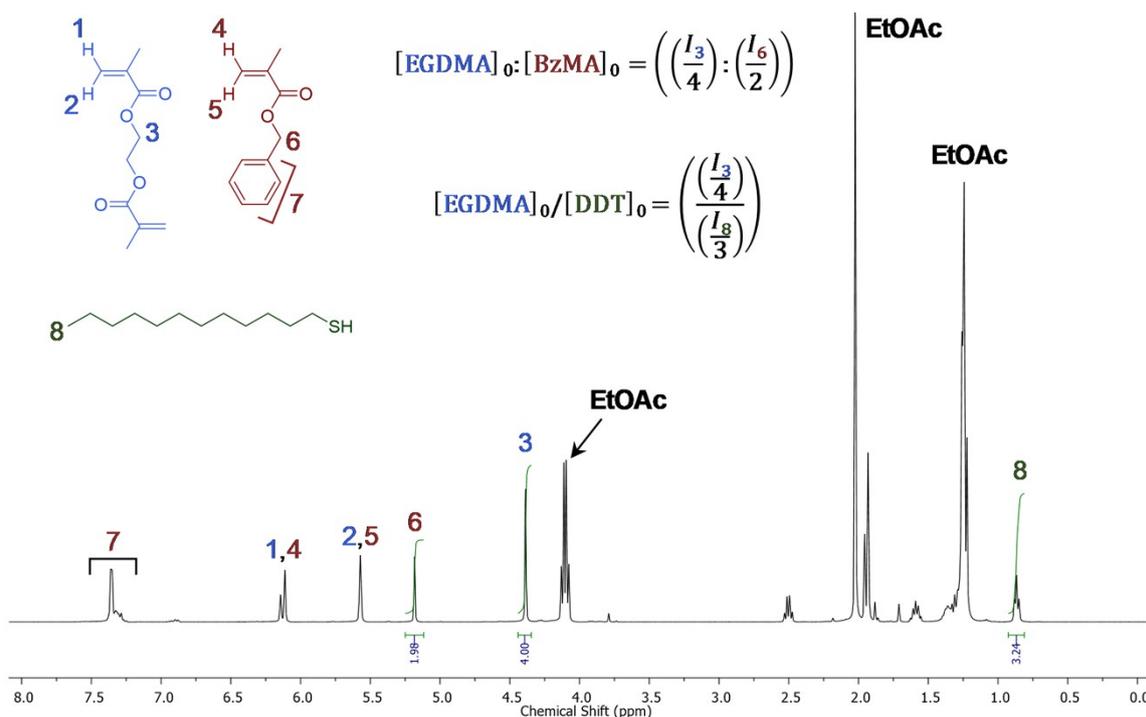


Figure S69 ^1H NMR (400 MHz, CDCl_3) spectrum obtained from the copolymerisation of EGDMA and BzMA with DDT, prior to thermal initiation ($t = 0$). The equations used to determine the initial ratio of EGDMA to DDT ($[\text{EGDMA}]_0/[\text{DDT}]_0$) and the initial molar ratio of EGDMA: BzMA ($[\text{EGDMA}]_0:[\text{BzMA}]_0$) are provided.

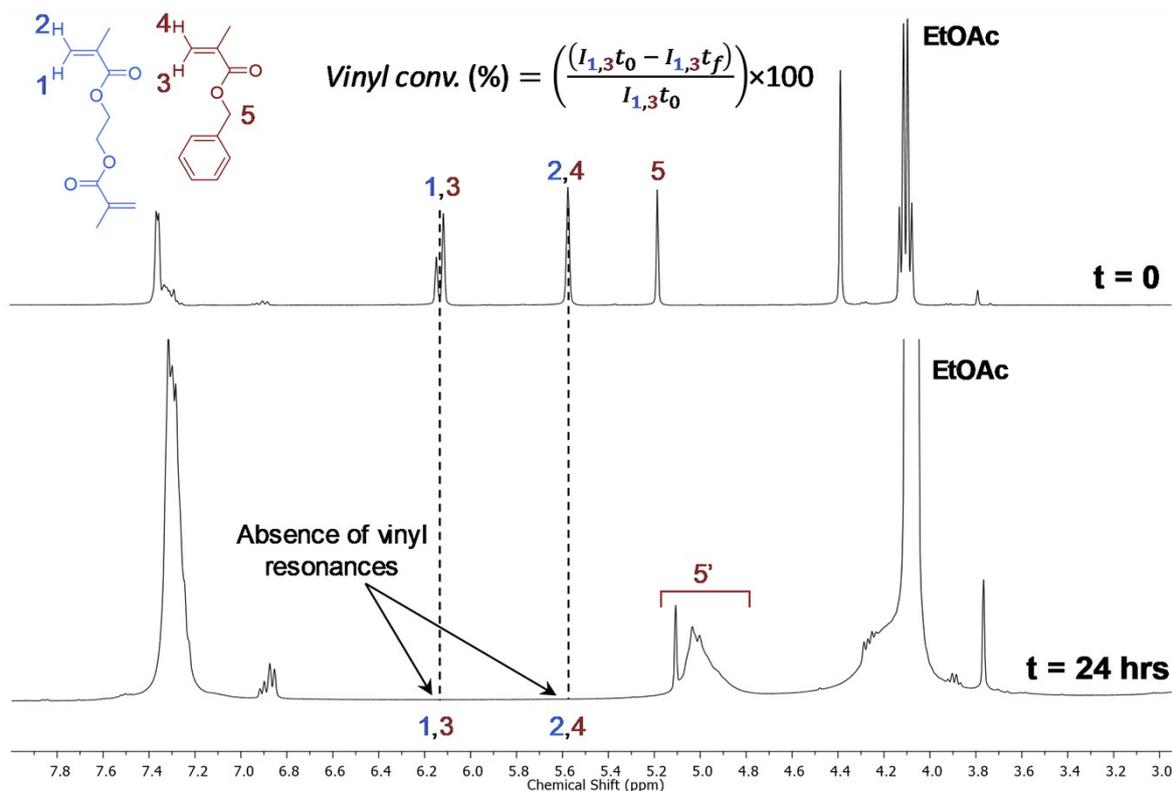


Figure S70 Overlaid ^1H NMR (400 MHz, CDCl_3) spectra obtained from the copolymerisation of EGDMA and BzMA with DDT, prior to thermal initiation (top) and 24 hours after initiation (bottom). The equation provided was used to determine monomer conversion (integrals normalised with respect to 5).

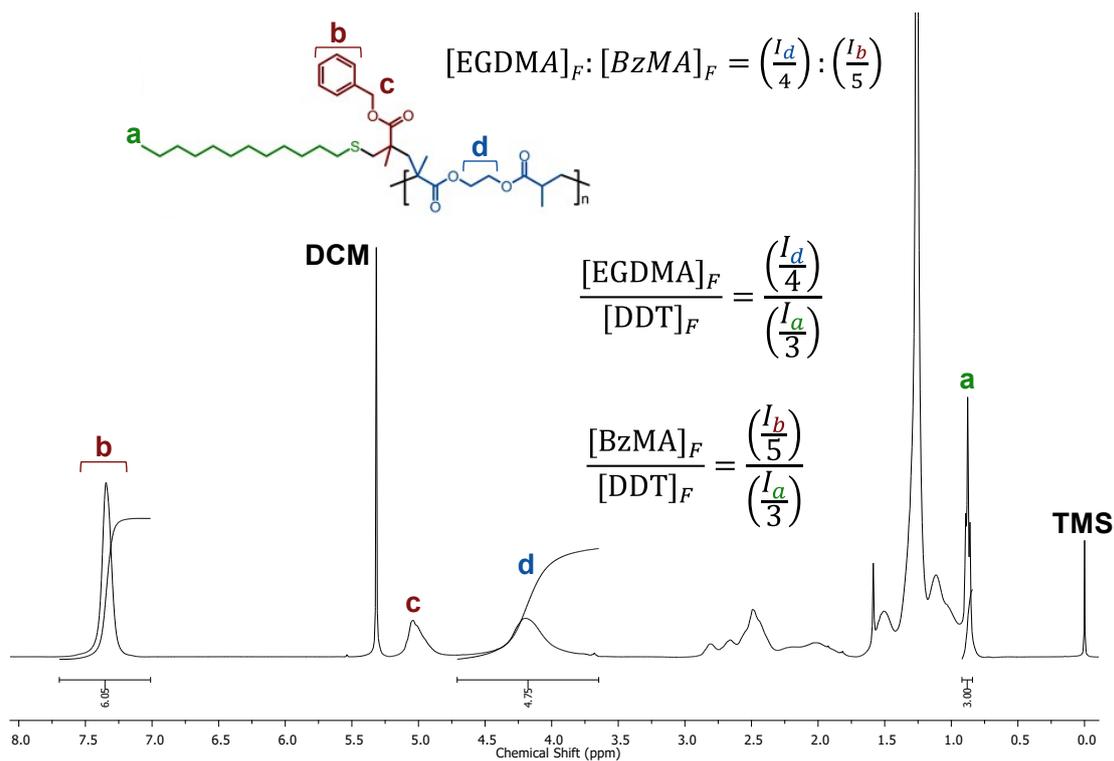


Figure S71 ^1H NMR spectrum (400 MHz, $\text{DCM-}d_2$) of $p([\text{DDT-EGDMA}]\text{-stat-BzMA})$ showing the calculations used to determine the final molar ratios of EGDMA to DDT ($[\text{EGDMA}]_F/[\text{DDT}]_F$) and EGDMA to BzMA in the purified polymer.

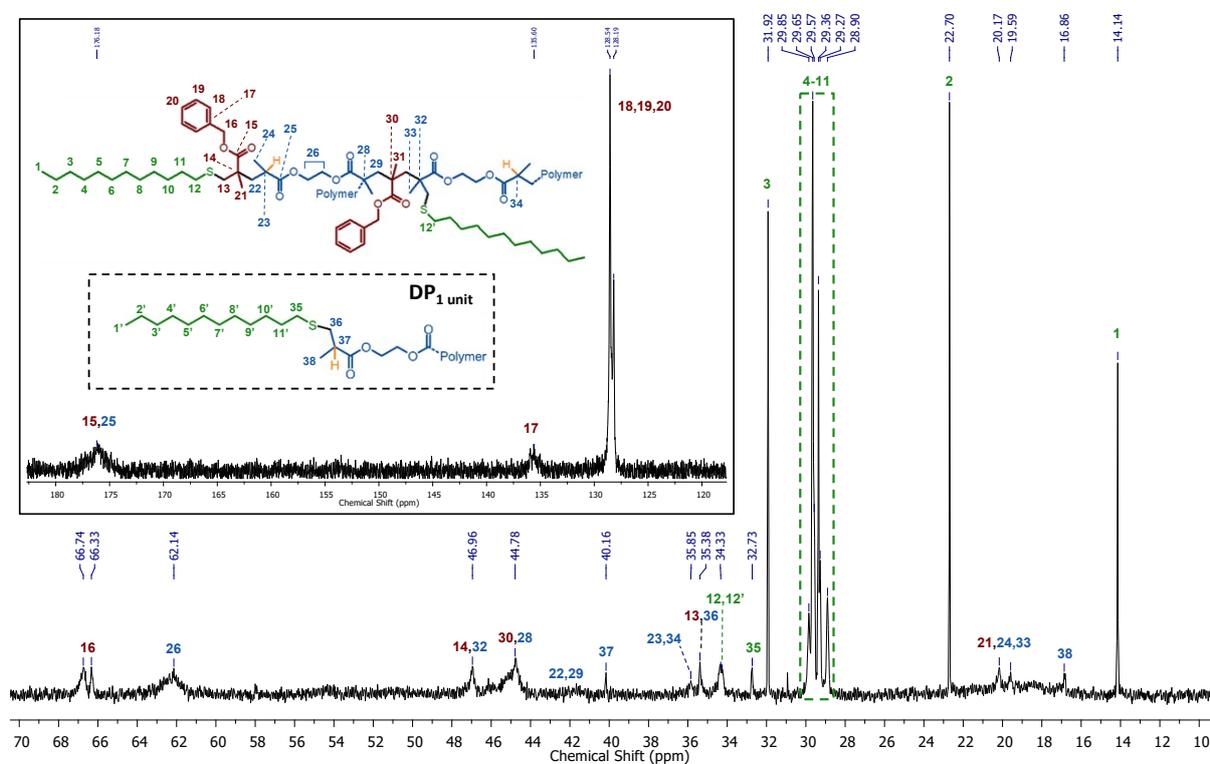


Figure S72 ^{13}C NMR (100 MHz, CDCl_3) spectrum of $p([\text{DDT-EGDMA}]\text{-stat-BzMA})$ including assignment of ^{13}C environments.

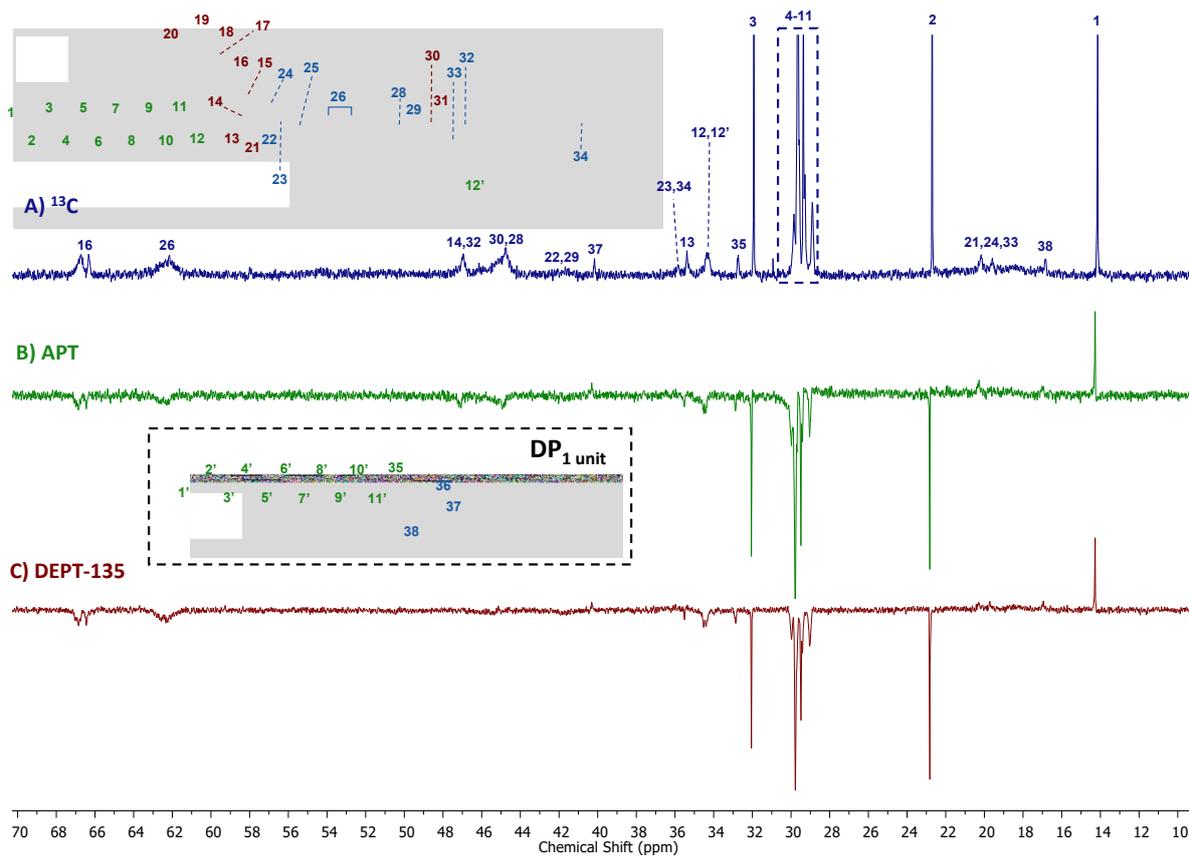


Figure S73 Overlaid A) ^{13}C , B) DEPT-135 and C) APT NMR (100 MHz, $CDCl_3$) spectra obtained for $p([DDT-EGDMA]-stat-BzMA)$ including assignment of ^{13}C environments.

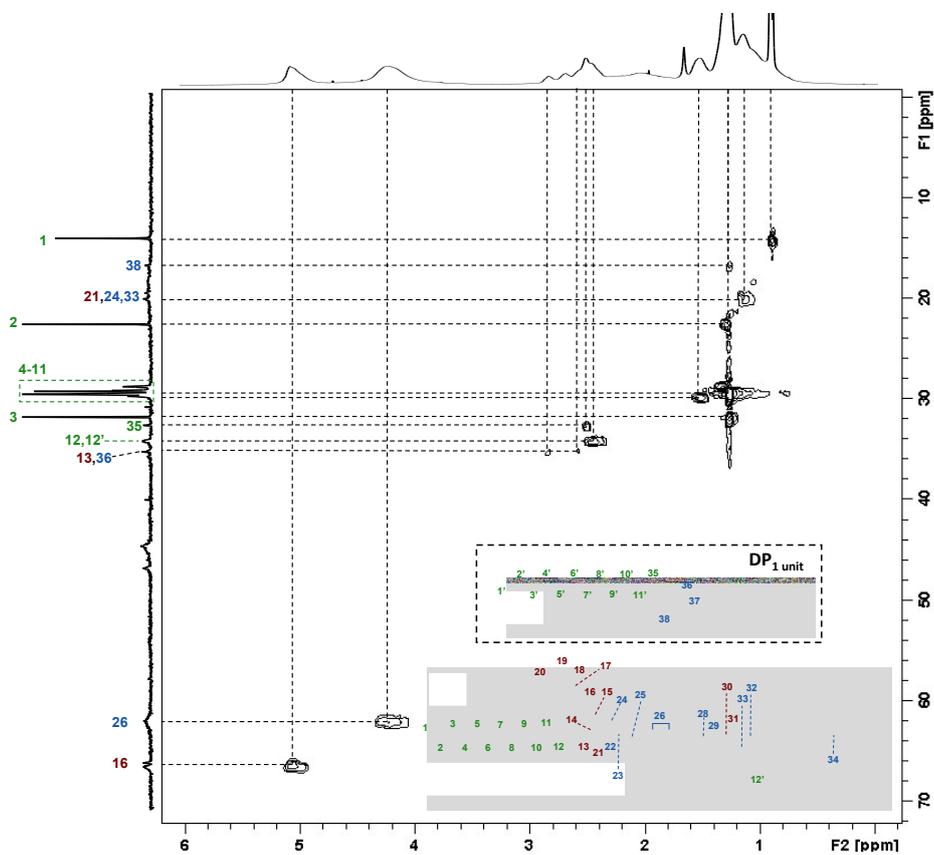


Figure S74 HSQC correlation of 1H and ^{13}C NMR spectra obtained from $p([DDT-EGDMA]-stat-BzMA)$, enabling assignment of several 1H and ^{13}C environments.

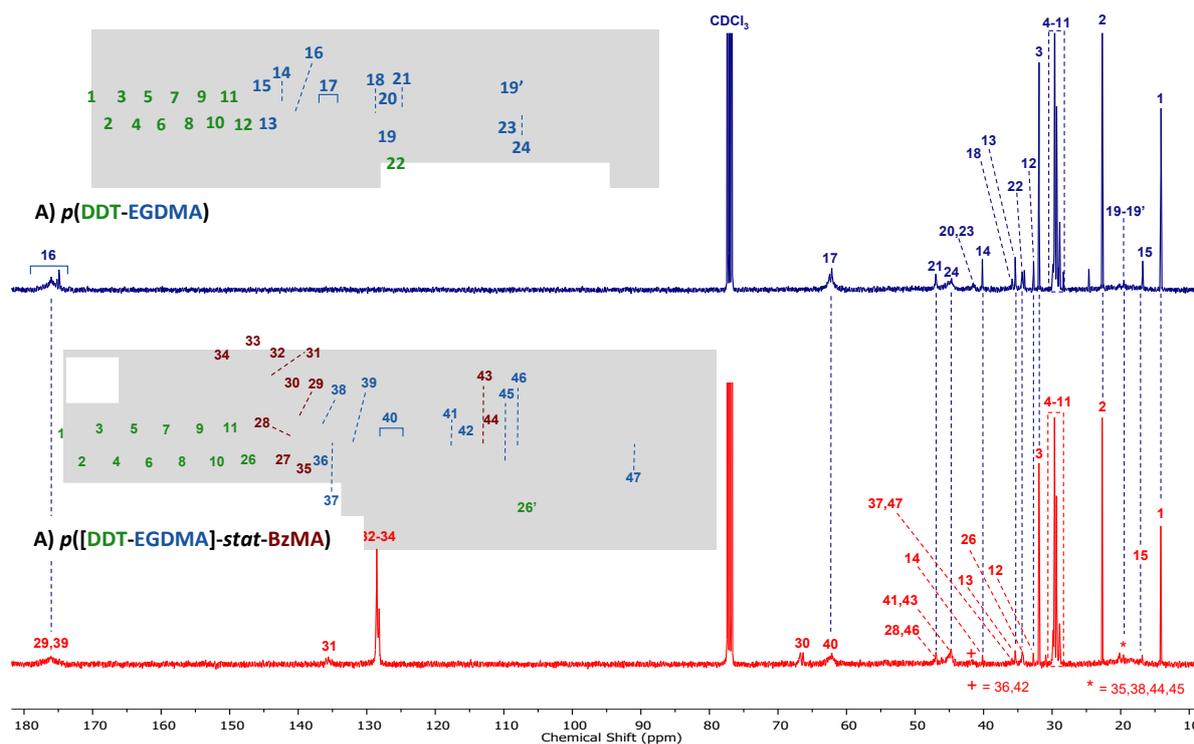


Figure S75 Overlaid ^{13}C NMR spectra (100 MHz, CDCl_3) obtained for A) $p(\text{DDT-EGDMA})$ and B) $p([\text{DDT-EGDMA}]\text{-stat-BzMA})$. This shows the presence of key structural units from $p(\text{DDT-EGDMA})$ repeat units (blue dashed lines) within the $p([\text{DDT-EGDMA}]\text{-stat-BzMA})$ NMR spectrum.

2.2.10 Synthesis & characterisation of $p([\text{tBuBzM-EGDMA}]\text{-stat-BzMA})$

EGDMA (5.00 g, 25.2 mmol, 0.925 equiv.), BzMA (4.44 g, 25.2 mmol, 0.925 equiv.), *t*BuBzM (4.92 g, 27.3 mmol, 1.000 equiv.) and AIBN (0.186 g, 1.14 mmol) were placed into a 50 mL round-bottom flask. Ethyl acetate (50 wt % based on EGDMA, BzMA and *t*BuBzM; 14.55 g, 16.13 mL) was added and the solution was deoxygenated using a nitrogen purge under magnetic stirring for 30 minutes. An aliquot (~100 μL) of the mixture was taken for determination of the initial molar ratios of: (i) EGDMA to *t*BuBzM ($[\text{EGDMA}]_0/[\text{tBuBzM}]_0$) and (ii) EGDMA to BzMA ($[\text{EGDMA}]_0/[\text{BzMA}]_0$) by ^1H NMR analysis (Figure S77). The flask was then placed in an oil bath at 70 $^\circ\text{C}$ for 24 hours. The reaction was stopped *via* cooling and exposure to air. An aliquot (~100 μL) of the reaction mixture was taken for determination of monomer conversion *via* ^1H NMR (Figure S78). The reaction mixture was then diluted in THF and precipitated into methanol twice (using a good solvent: anti-solvent volume ratio of 1:20) at ambient temperature, yielding a white precipitate. The polymer was dried *in vacuo* at 40 $^\circ\text{C}$ overnight to yield $p([\text{tBuBzM-EGDMA}]\text{-stat-BzMA})$ as a white powder. The product was analysed by TD-SEC (Figure S76) and several ^1H and ^{13}C NMR spectroscopic techniques (Figure S79-S83).

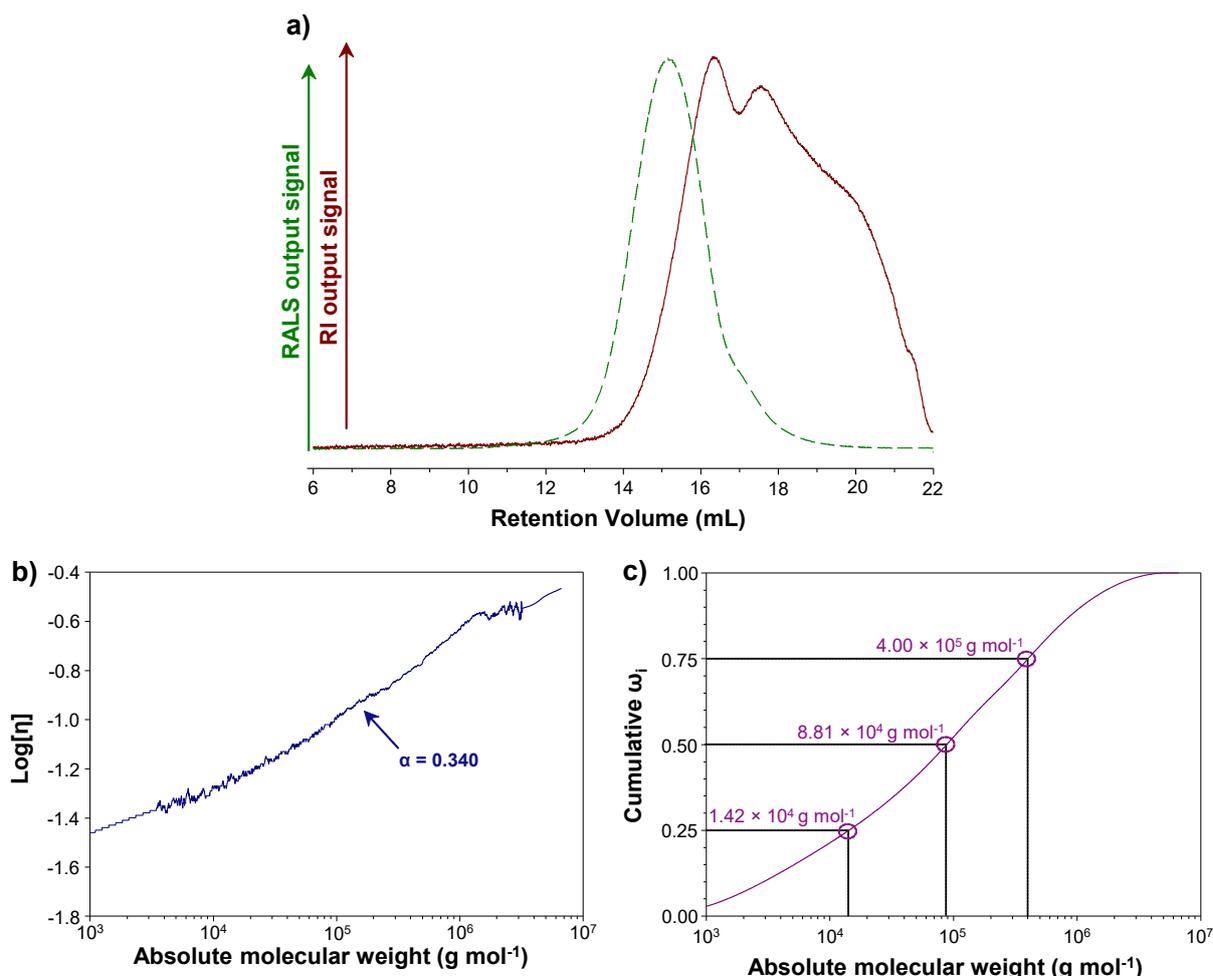


Figure S76 TD-SEC analysis of *p*(*t*BuBzM-EGDMA-*stat*-BzMA). a) Overlaid RI (red solid line) and RALS (green dashed line) chromatograms. b) Evaluation of copolymer topological structure via MHS analysis. c) Analysis of the relationship between absolute molecular weight and the cumulative weight fraction.

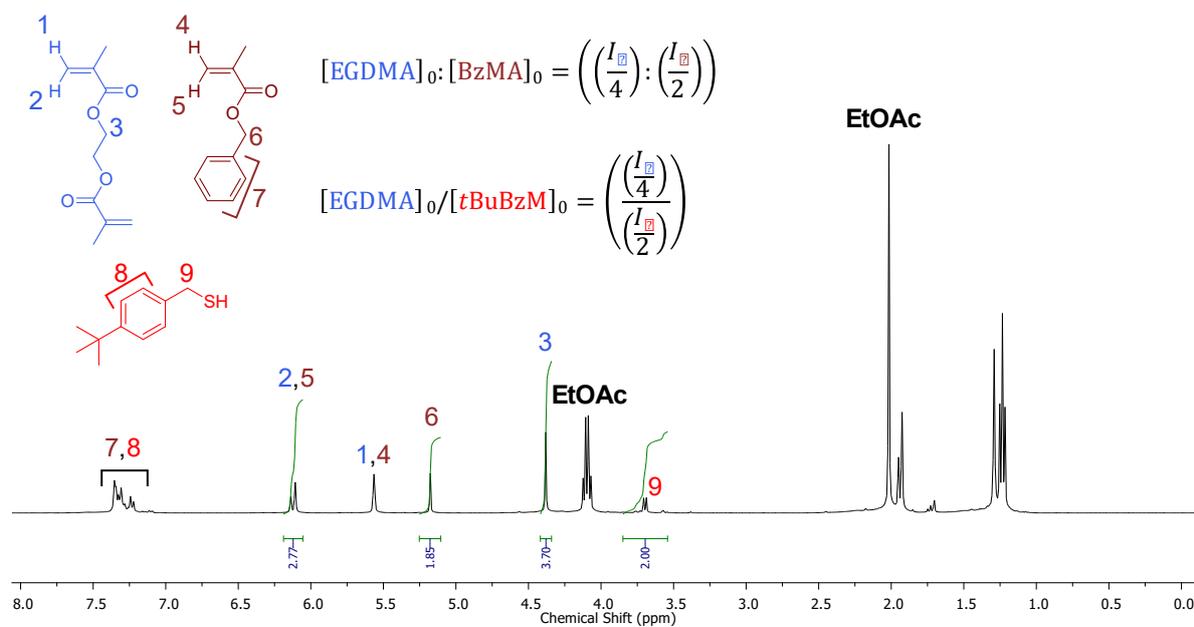


Figure S77 ^1H NMR (400 MHz, CDCl_3) spectrum obtained from the copolymerisation of EGDMA and BzMA with *t*BuBzM, prior to thermal initiation ($t = 0$). The equations used to determine the initial molar ratios of EGDMA to *t*BuBzM ($[\text{EGDMA}]_0 / [t\text{BuBzM}]_0$) and EGDMA to BzMA ($[\text{EGDMA}]_0 : [\text{BzMA}]_0$) are provided.

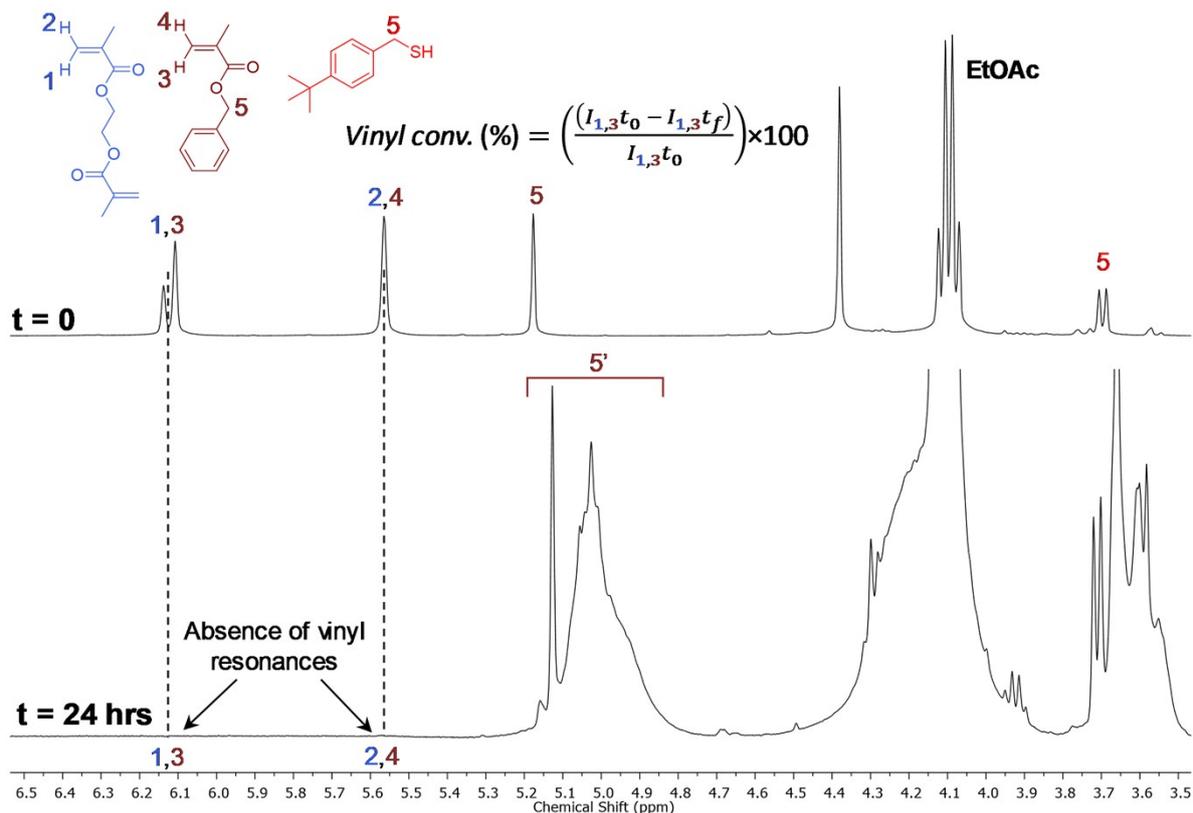


Figure S78 Overlaid ^1H NMR (400 MHz, CDCl_3) spectra obtained from the copolymerisation of EGDMA and BzMA with *t*BuBzM, prior to thermal initiation (top) and 24 hours after initiation (bottom). The equation provided was used to determine monomer conversion (integrals normalised with respect to 5).

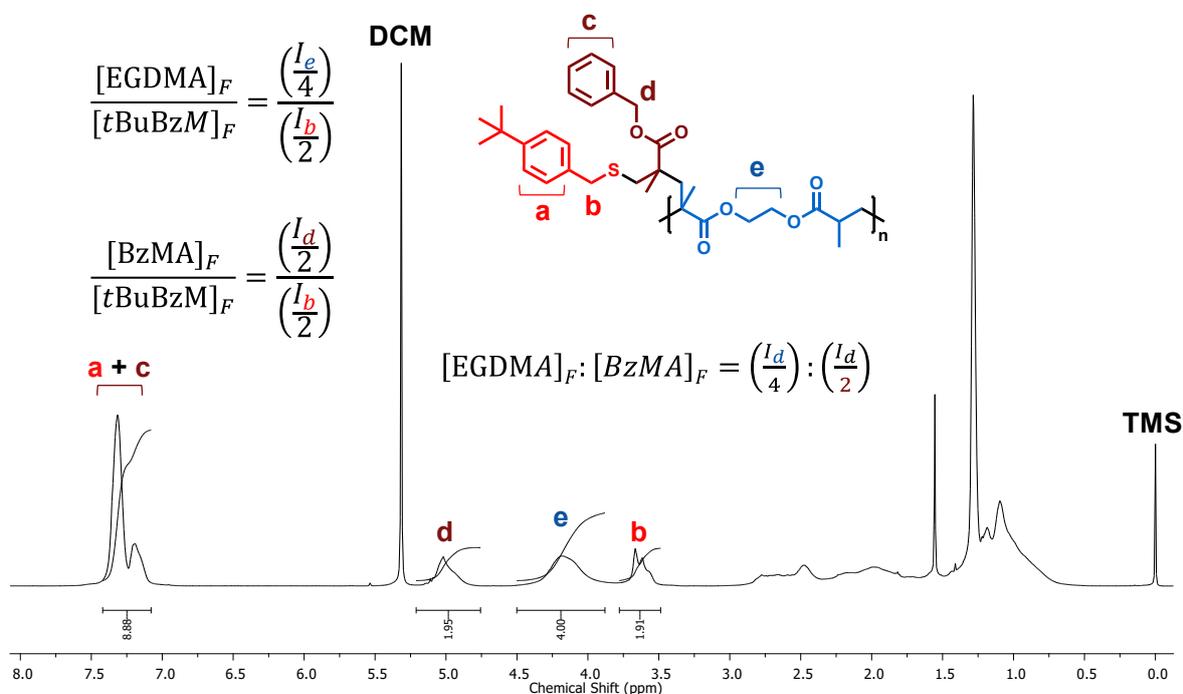


Figure S79 ^1H NMR spectrum (400 MHz, DCM-d_2) of $p([t\text{BuBzM-EGDMA}]_{\text{stat}}\text{-BzMA})$ showing the calculations used to determine the final molar ratios of EGDMA to *t*BuBzM ($[\text{EGDMA}]_F/[\text{tBuBzM}]_F$) and EGDMA to BzMA in the purified polymer.

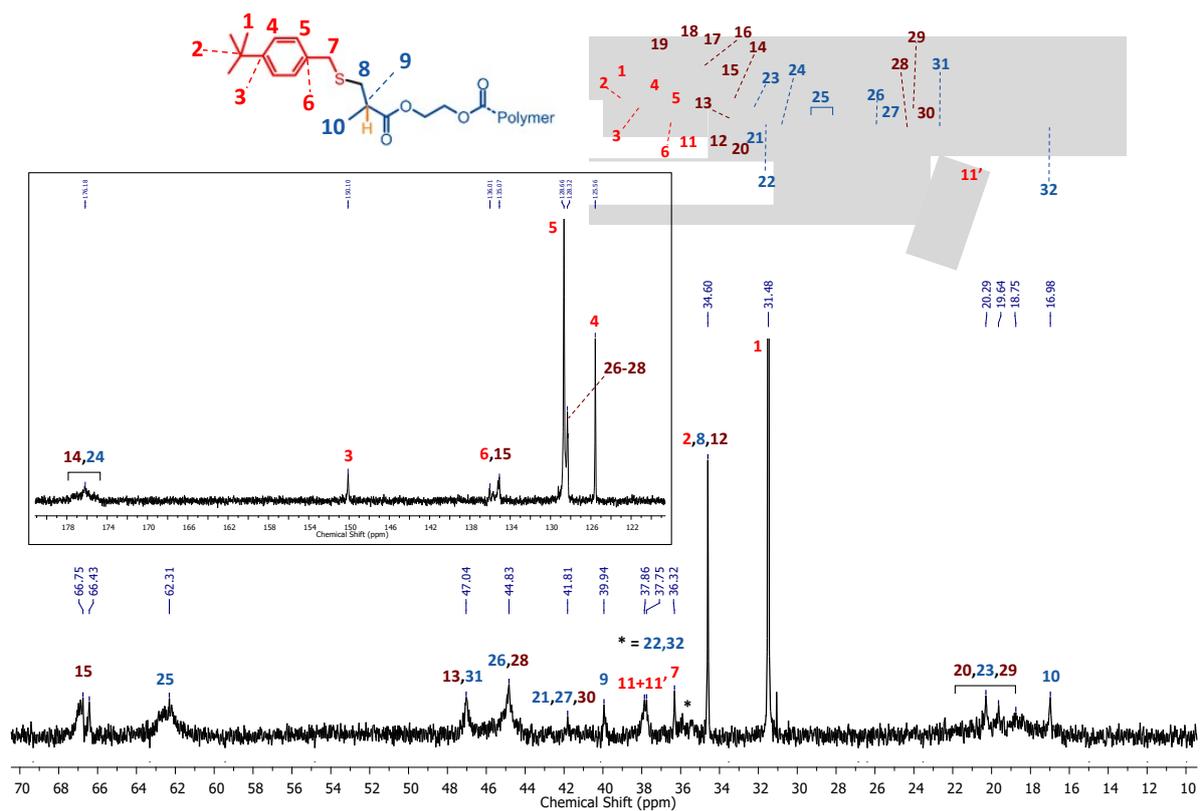


Figure S80 ^{13}C NMR (100 MHz, CDCl_3) spectrum of $p([t\text{BuBzM-EGDMA}]\text{-stat-BzMA})$ including assignment of ^{13}C environments.

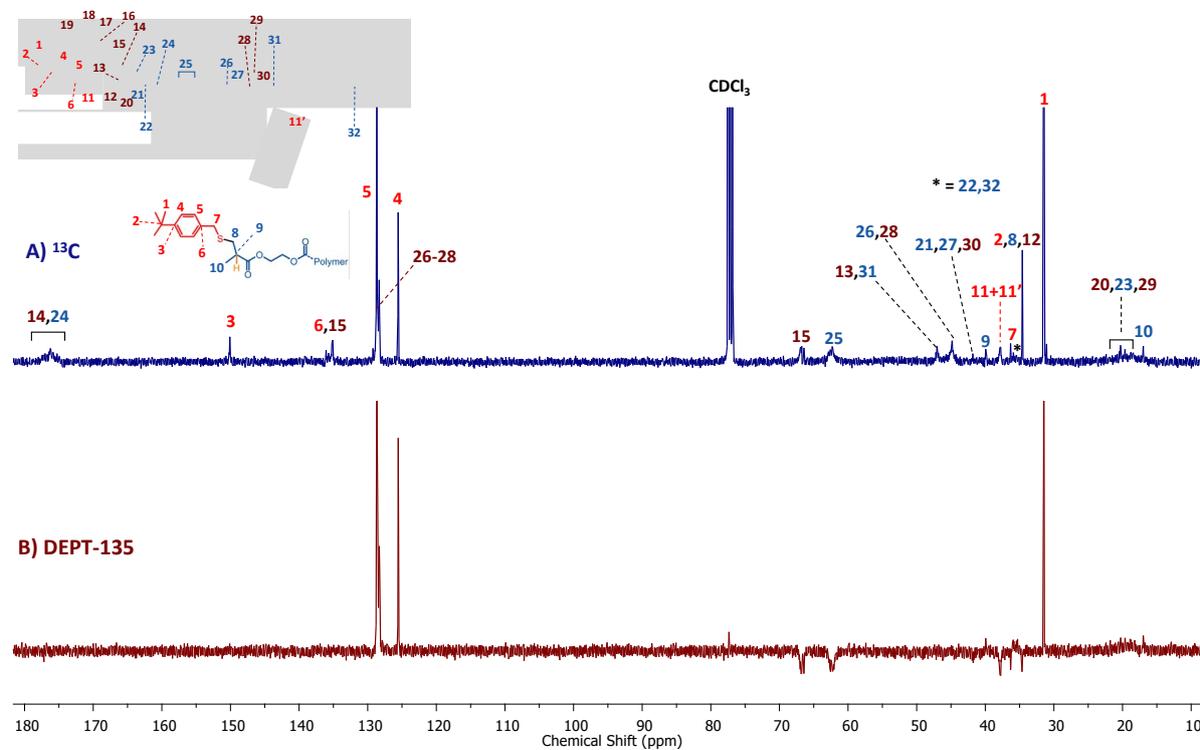


Figure S81 Overlaid A) ^{13}C , B) DEPT-135 and C) APT NMR (100 MHz, CDCl_3) spectra obtained for $p([t\text{BuBzM-EGDMA}]\text{-stat-BzMA})$ including assignment of ^{13}C environments.

Copolymer	¹ H NMR											TD-SEC				DSC
	DDT ^a χ_0	<i>t</i> BuBzM ^a χ_0	EGDMA ^a χ_0	BPADMA ^a χ_0	$\Sigma[\text{MVT}]_0/$ $\Sigma[\text{Tel}]_0^a$	Conv. ^b (%)	DDT ^c χ_F	<i>t</i> BuBzM ^c χ_F	EGDMA ^c χ_F	BPADMA ^c χ_F	$\Sigma[\text{MVT}]_F/$ $\Sigma[\text{Tel}]_F^c$	M_w^d (g mol ⁻¹)	M_n^d (g mol ⁻¹)	\bar{D}^d	α^d	T_g^e
<u>Mixed Telogen Copolymers</u>																
<i>p</i> [(<i>t</i> BuBzM-EGDMA)- <i>stat</i> -(DDT-EGDMA)]	0.50	0.50	1.00	0.00	0.83	>99	0.51	0.49	1.00	0.00	1.04	578,003	13,546	42.67	0.351	-1
<i>p</i> [(<i>t</i> BuBzM-BPADMA)- <i>stat</i> -(DDT-BPADMA)]	0.50	0.50	0.00	1.00	0.40	>99	0.47	0.53	0.00	1.00	1.14	441,016	12,081	36.50	0.333	39
<u>Mixed Tagogen Copolymers</u>																
<i>p</i> [(DDT-BPADMA)- <i>stat</i> -(DDT-EGDMA)]	1.00	0.00	0.51	0.49	0.50	>99	1.00	0.00	0.52	0.48	1.06	1,557,000	31,902	49.78	0.369	-14
<i>p</i> [(<i>t</i> BuBzM-BPADMA)- <i>stat</i> -(<i>t</i> BuBzM-EGDMA)]	0.00	1.00	0.50	0.50	0.55	>99	0.00	1.00	0.48	0.52	1.05	5,326,000	56,718	93.90	0.496	48

Table S4 Characterisation of mixed telogen and mixed MVT statistical copolymers synthesised *via* TBRT

^aDetermined *via* ¹H NMR analysis of the reaction mixture prior to initiation. ^bDetermined *via* ¹H NMR analysis of the reaction mixture after 24 hours. ^cDetermined *via* ¹H NMR analysis of the purified copolymer.

^dDetermined *via* TD-SEC analysis of the purified copolymer at 35°C in THF. ^eDetermined *via* DSC of the purified copolymers following removal of their thermal history.

Copolymer	¹ H NMR											TD-SEC				DSC
	DDT ^a χ_0	<i>t</i> BuBzM ^a χ_0	EGDMA ^a χ_0	BzMA ^a χ_0	$\Sigma[\text{MVT}]_0/$ $\Sigma[\text{Tel}]_0^a$	Conv. ^b (%)	DDT ^c χ_F	<i>t</i> BuBzM ^c χ_F	EGDMA ^c χ_F	BzMA ^c χ_F	$\Sigma[\text{MVT}]_F/$ $\Sigma[\text{Tel}]_F^c$	M_w (g mol ⁻¹) ^d	M_w (g mol ⁻¹) ^d	\bar{D}^d	α^d	T_g^e
<u>Mixed mono-vinyl/MVT Copolymers</u>																
<i>p</i> [(DDT-EGDMA)- <i>stat</i> -BzMA]	1.00	0.00	0.50	0.50	0.93	>99	1.00	0.00	0.50	0.50	1.19	2,149,000	27,694	77.59	0.401	12
<i>p</i> [(<i>t</i> BuBzM-EGDMA)- <i>stat</i> -BzMA]	0.00	1.00	0.50	0.50	0.93	>99	0.00	1.00	0.49	0.51	1.05	361,208	8,143	16.49	0.340	33

Table S5 Characterisation of mixed mono-vinyl and MVT statistical copolymers synthesised *via* TBRT

^aDetermined *via* ¹H NMR analysis of the reaction mixture prior to initiation. ^bDetermined *via* ¹H NMR analysis of the reaction mixture after 24 hours. ^cDetermined *via* ¹H NMR analysis of the purified copolymer.

^dDetermined *via* TD-SEC analysis of the purified copolymer at 35°C in THF. ^eDetermined *via* DSC of the purified copolymers following removal of their thermal history.

3.2 Mixed taxogen copolymers

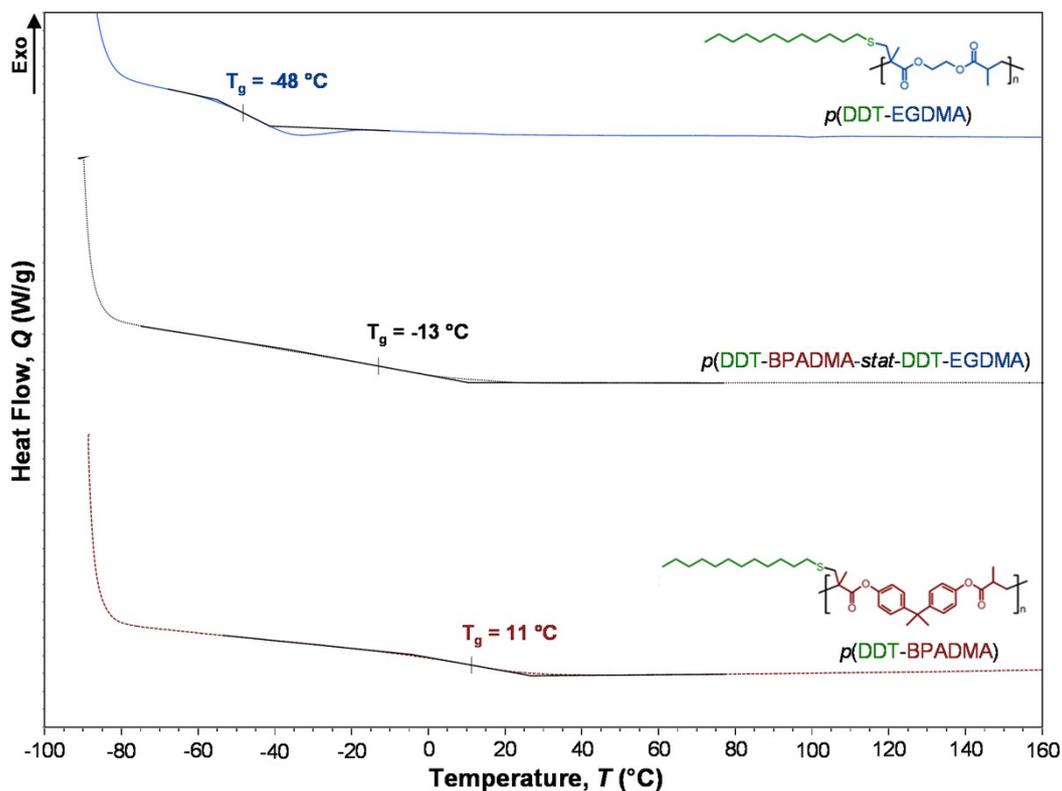


Figure S86 Analysis of the impact of (co)polymer structure on the T_g of mixed taxogen branched copolymers. Overlaid DSC thermograms obtained for $p(\text{DDT-EGDMA})$ (top, blue solid line), $p(\text{DDT-BPADMA-stat-DDT-EGDMA})$ (centre, black dotted line) and $p(\text{DDT-BPADMA})$ (bottom, dashed maroon line).

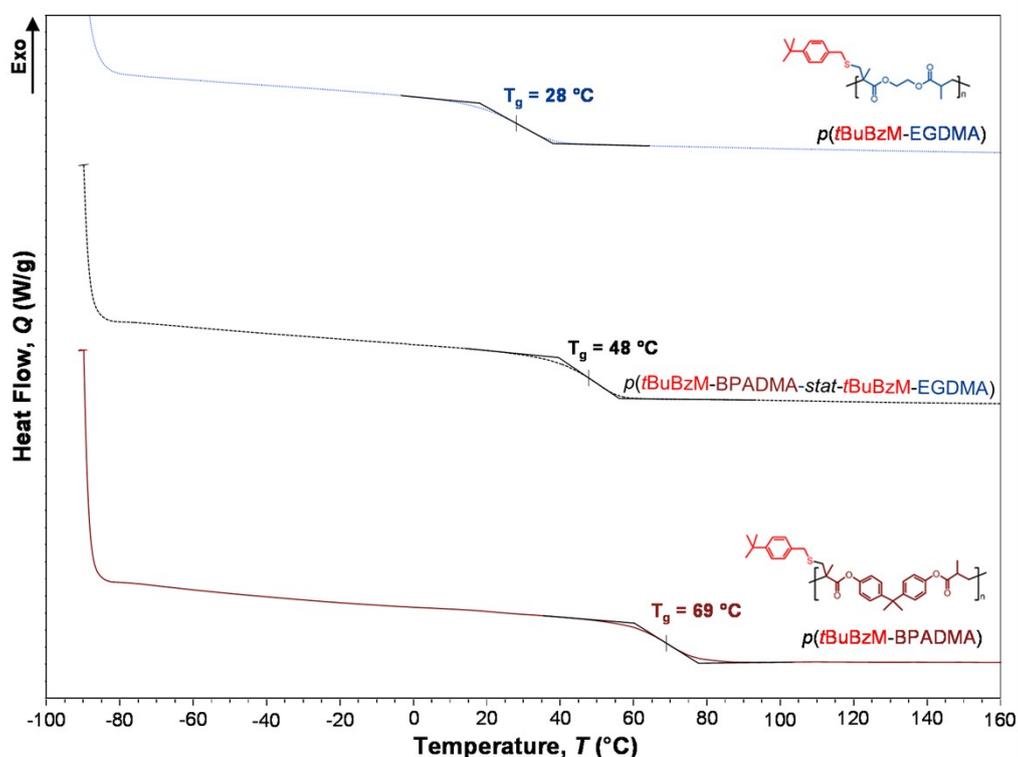


Figure S87 Analysis of the impact of (co)polymer structure on the T_g of mixed taxogen copolymers. Overlaid DSC thermograms obtained for $p(t\text{BuBzM-EGDMA})$ (top, blue dotted line), $p(t\text{BuBzM-EGDMA-stat-tBuBzM-BPADMA})$ (centre, black dashed line) and $p(t\text{BuBzM-BPADMA})$ (bottom, solid maroon line).

3.3 Mono-vinyl monomer-containing copolymers

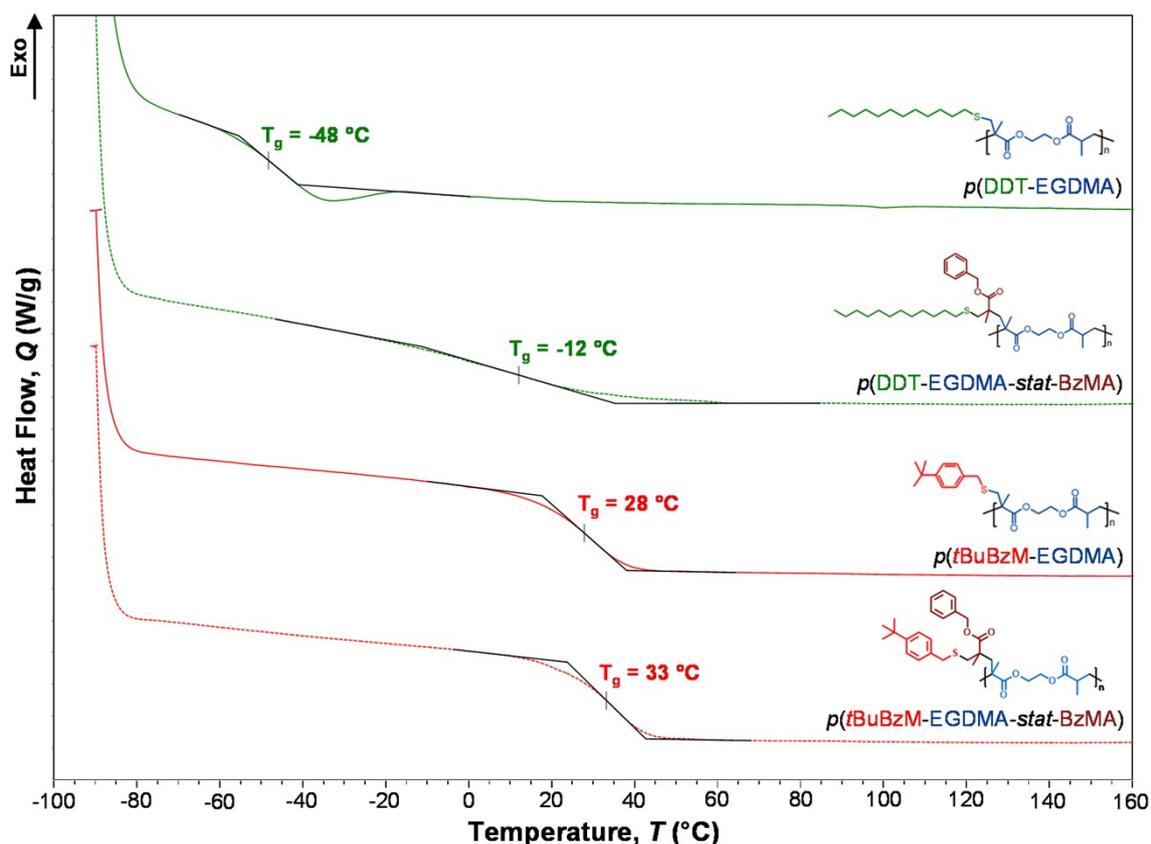


Figure S88 Analysis of the impact of (co)polymer structure on the T_g . Overlaid DSC thermograms obtained for $p(\text{DDT-EGDMA})$ (top, green solid line), $p(\text{DDT-EGDMA-stat-BzMA})$ (green dashed line), $p(\text{tBuBzM-EGDMA})$ (solid red line) and $p(\text{tBuBzM-EGDMA-stat-BzMA})$ (bottom, dashed red line).

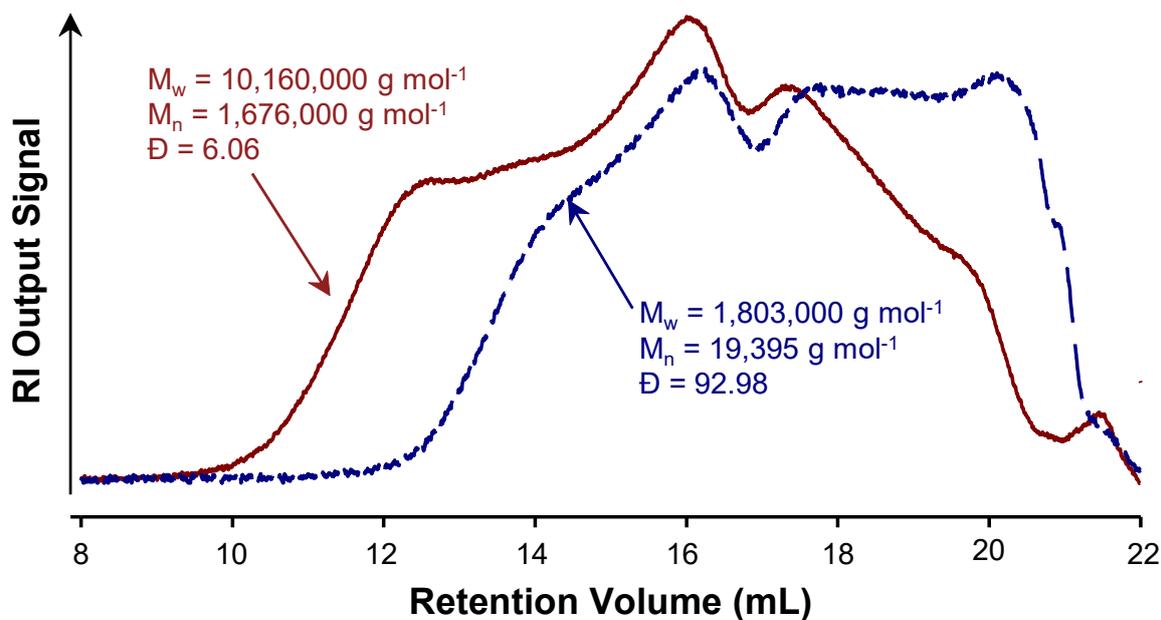


Figure S89 Overlaid TD-SEC chromatograms obtained for $p(\text{DDT-EGDMA})$ samples possessing varied molecular weight distributions, following purification *via* single (blue) and multiple (red) precipitations in methanol.

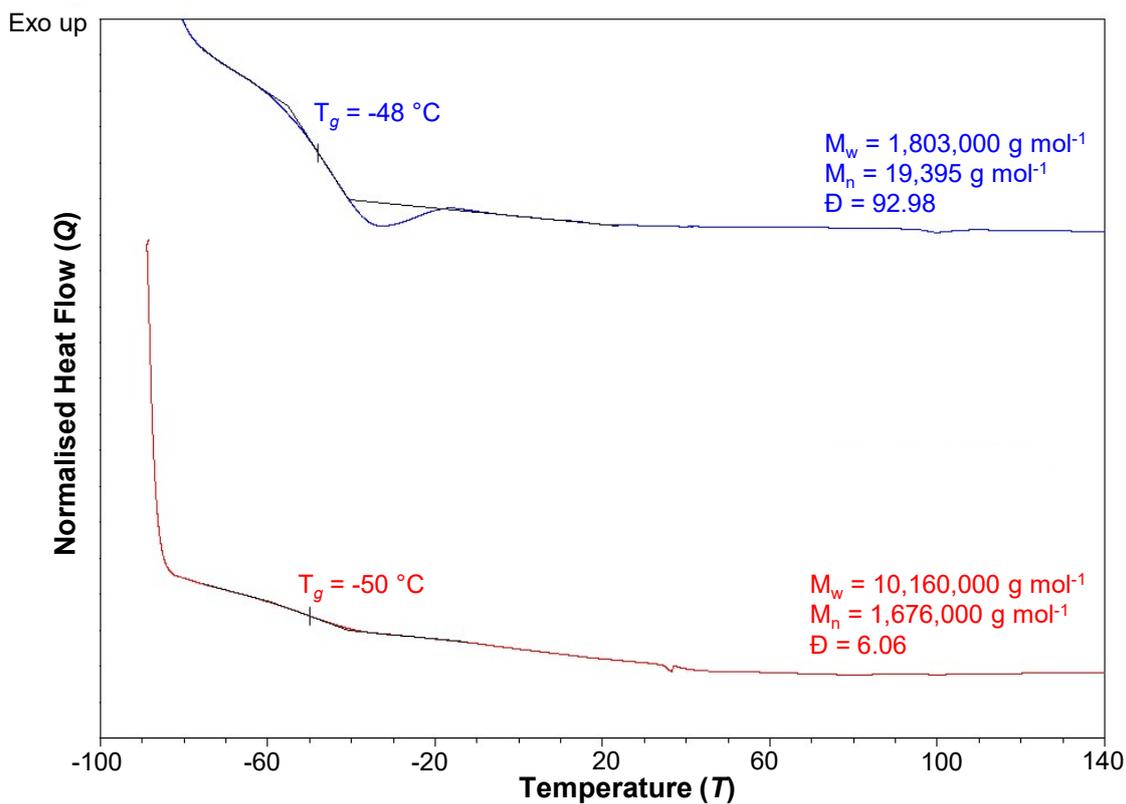


Figure S90 Analysis of the impact of molecular weight on the T_g of *p*(DDT-EGDMA). Overlaid DSC thermograms obtained for *p*(DDT-EGDMA) samples containing number-average molecular weights of $19,395 \text{ g mol}^{-1}$ (top, blue) and $1,676,000 \text{ g mol}^{-1}$ (bottom, red).

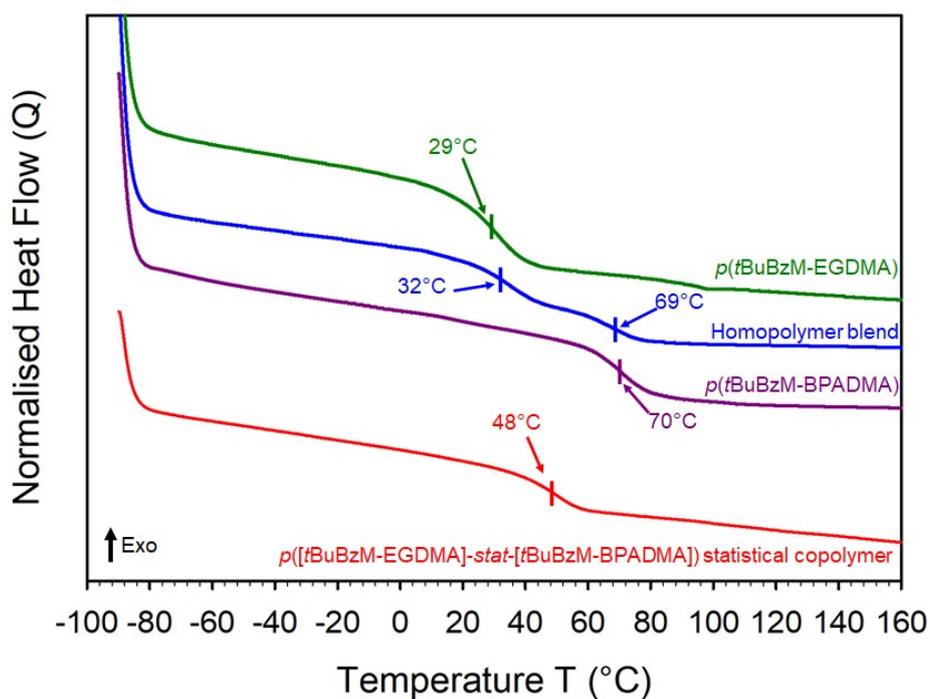


Figure S91 Comparison of TBRT homopolymers, blends and mixed MVT statistical copolymer thermal behaviour. Overlaid DSC thermograms obtained for two homopolymers - *p*(*t*BuBzM-EGDMA) (green) and *p*(*t*BuBzM-BPADMA) (purple), a physical blend of these homopolymers (blue) and a *p*([*t*BuBzM-EGDMA]-*stat*-[*t*BuBzM-BPADMA]) mixed MVT statistical copolymer (red). The physical blend (blue) shows two thermal transitions that correspond to the component homopolymers whilst the mixed MVT statistical copolymer shows a single transition that lays between the corresponding homopolymer values.

4. References

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