Novel hyperbranched polymers from Transfer-dominated Branching Radical Telomerisation (TBRT) of diacrylate taxogens

Samuel Mckeating,[a,b] Corinna Smith,[a,b] Oliver Penrhyn-Lowe,[a,b] Sean Flynn,[a,b] Stephen Wright,[a,b] Pierre Chambon,[a,b] Andrew Dwyer[a,b] and Steve Rannard [a,b,*]

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

[b.]Materials Innovation Factory, University of Liverpool, Crown Street, L69 7ZD, UK

Corresponding Author E-mail: srannard@liv.ac.uk

Electronic Supplementary Information

Experimental

Materials

1,4 butanediol diacrylate (BDA, 97 %) and 1,6 hexanediol diacrylate (HDA, 98 %) were purchased from TCI chemicals. 1,4 butanediol dimethacrylate (BDMA, 98 %), 1,6 hexanediol dimethacrylate (HDMA, 98 %), butyl acrylate (98 %), butyl methacrylate (98 %), 1-dodecanethiol (DDT, > 98 %), 2,2'-azobis(2-methylpropionitrile) (AIBN, 98%) and deuterated chloroform (CDCl3, 99.8 atom% D) were purchased from Sigma Aldrich. Tetrahydrofuran (THF, HPLC-grade), methanol (MeOH, analytical grade) and toluene (analytical grade) were purchased from Fischer. All materials were used as received unless otherwise stated.

Methods

^{1}H NMR spectra were recorded on a Bruker Advance DPX-400 MHz spectrometer. Samples were analysed in deuterated chloroform (CDCl3) at ambient temperature. Chemical shifts (δ) are reported in parts per million (ppm) relative to the known solvent signal (δ = 7.26 ppm). All TD-SEC analysis of branched polymers was performed using an Agilent 1260 Infinity ii instrument, with multi detector suite consisting of: 1260 Infinity II Isocratic Pump (G7110B) with integrated 2-channel degasser, 1260 Infinity II Vialsampler (G7129A), 1260 Infinity II Multicolumn Thermostat MCT (G7116A), 1260 Infinity II GPC MDS System (G7800A) housing a Refractive Index Detector, Viscometer, and Dual-angle Light Scattering Detector and a 1260 Infinity II Variable Wavelength Detector (G7114A). The two columns in utility were PLgel MIXED Guard Column, 7.5 x 50 mm, 10 µm and PLgel MIXED-B Analytical Column, 7.5 x 300 mm, 10 µm (x2 – run in series). A mobile phase of THF 35 °C was used at a flow rate of 1 mL/min. All samples were dissolved at 10 mg/mL in the eluent and filtered through a 0.2 µm PTFE syringe filter prior to injection (100 µL). Narrow and broad polystyrene standards were used as calibrants. SEC analysis of linear telomers was performed using an Agilent system with the same specifications as above, but instead utilising a Malvern Viscotek column set consisting of a T1000 column and a T2000 column in series. A mobile phase of THF 35 °C was used at a flow rate of 1 mL/min. All samples were dissolved at 10 mg/mL in the eluent and filtered through a 0.2 µm PTFE syringe filter prior to injection (100 µL). All SEC associated data were estimated using Agilent GPC/SEC Software Version 2.2.

Synthetic procedures

TBRT reaction

In a typical TBRT experiment, HDA, BDA, BDMA or HDMA, (x molar equiv.), DDT (1 molar equiv.), AIBN (1.5 mol % per double bond relative to vinyl monomer concentration) and EtOAc/Toluene (50 wt. % solids) were loaded into a 25 mL round-bottomed flask equipped with a magnetic stirrer bar. The molar ratio of taxogen to telogen (DDT) was adjusted for each taxogen used until a critical gelation point was reached. The solution was homogenised by agitation and a sample was extracted for ^{1}H NMR spectroscopic analysis prior to initiation. The solution was deoxygenated whilst stirring for 20 minutes using a nitrogen purge. The solution was then heated to 70 °C (EtOAc) or 100 °C (Toluene) with stirring and allowed to proceed for 24 hours. The reaction was ceased by exposure to air and cooling to ambient temperature. A sample of the crude reaction mixture was extracted for ^{1}H NMR spectroscopic analysis. The remaining sample was diluted with THF (< 10 mL) to reduce the viscosity, and precipitated into cold methanol or IPA (depending on the telogen used). Precipitations typically afforded a white precipitate and turbid supernatant. The precipitate was washed further with fresh methanol (3 x 50 mL) and subsequently dried *in vacuo* overnight at 40 °C. Finally, samples of the purified polymer were taken for 1H NMR and TD-SEC analysis.

Determining TBRT reaction kinetics

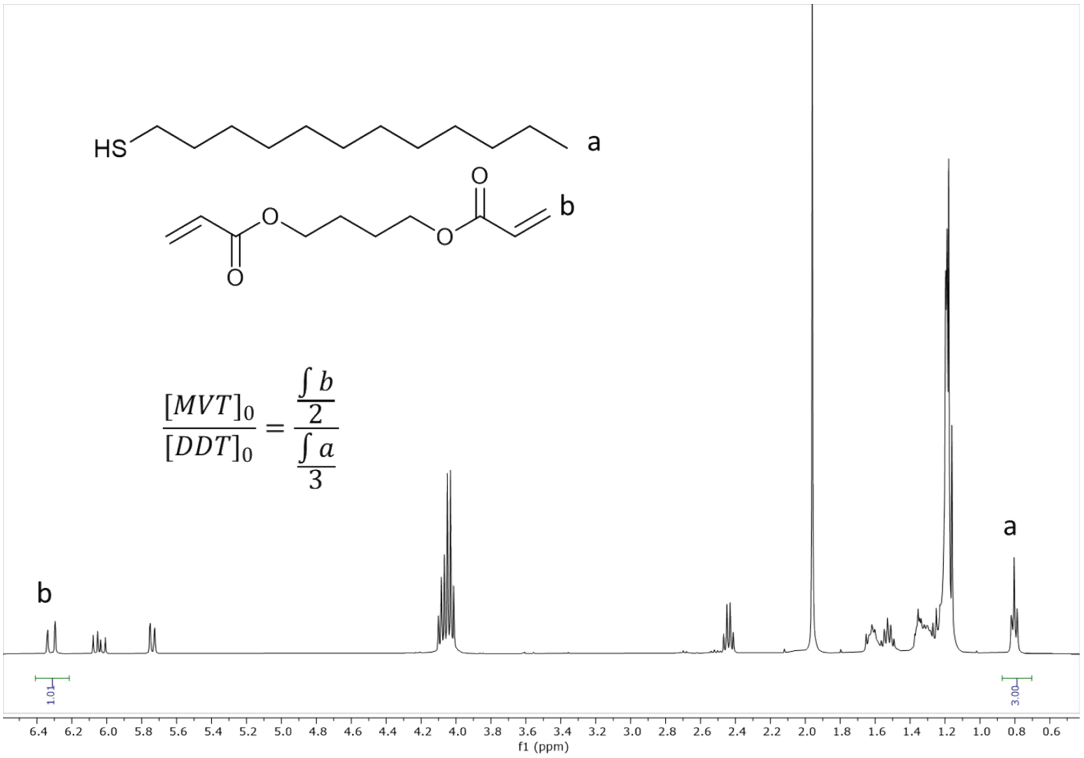
HDA, BDA, BDMA or HDMA, (x molar equiv.), DDT (1 molar equiv.), AIBN (1.5 mol% per double bond equiv.) and EtOAc, (50wt%) were added into a 25mL round bottomed flask. A nitrogen blanket was added to the reaction mixture and was maintained throughout the reaction. A crude sample was taken at t=0 for analysis by 1H NMR. The solution was then heated at 70^{o}C under magnetic stirring. For acrylic taxogens, samples were taken every 2 minutes until 30 minutes had elapsed. For methacrylic taxogens, samples were taken every 10 minutes for 1 hour and then every 15 minutes until 3 hours had elapsed. Each sample was extracted and rapidly cooled on ice to prevent further monomer conversion. Crude samples were analysed by ^{1}H NMR spectroscopy to determine vinyl conversion.

Linear telomerisation of BuMA and BuA with DDT

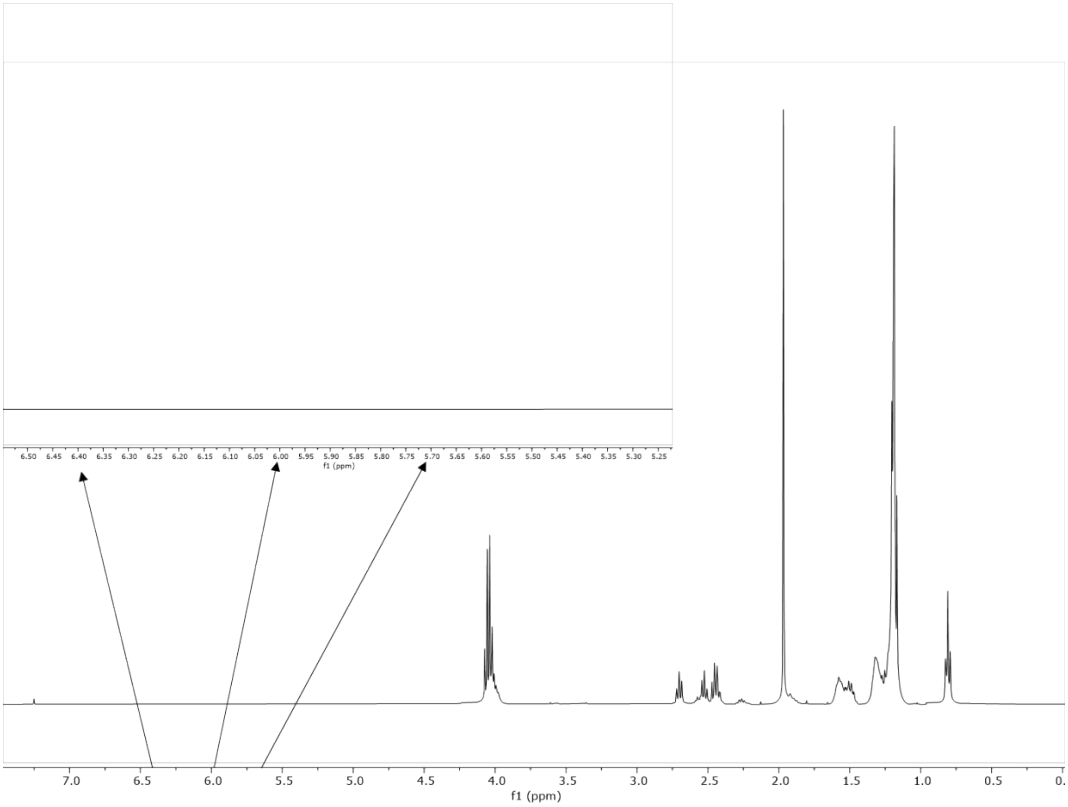
For the linear telomerisations of BuMA with DDT, BuMA (4.00 g, 28.13 mmol, 2 equiv.), DDT (2.85 g, 14.06 mmol, 1 equiv.), AIBN (69.3 mg, 0.42 mmol, 1.5 mol% equiv.) and toluene (6.85

g, 74.31 mmol, 50 wt%) were loaded into a 25 mL round-bottomed flask with homogenised *via* manual agitation. A sample was extracted for ^{1}H NMR spectroscopic analysis of the reaction mixture prior to initiation, and the solution was separated in equal volume into four 10 mL round bottomed flasks equipped with magnetic stirrer bars. The solutions were deoxygenated whilst stirring for 15 minutes using a nitrogen sparge and each then heated to a temperature of 70 °C, 80 °C, 90 °C, or 100 °C with stirring and the reactions allowed to proceed for 24 hours under a nitrogen atmosphere. The reactions were ceased by exposure to air and cooling to ambient temperature. A sample of each crude reaction mixture was extracted for ^{1}H NMR spectroscopic analysis. The crude samples were concentrated *in vacuo* using a spiral evaporator at 50 °C to remove the toluene. All samples were then analysed by SEC.

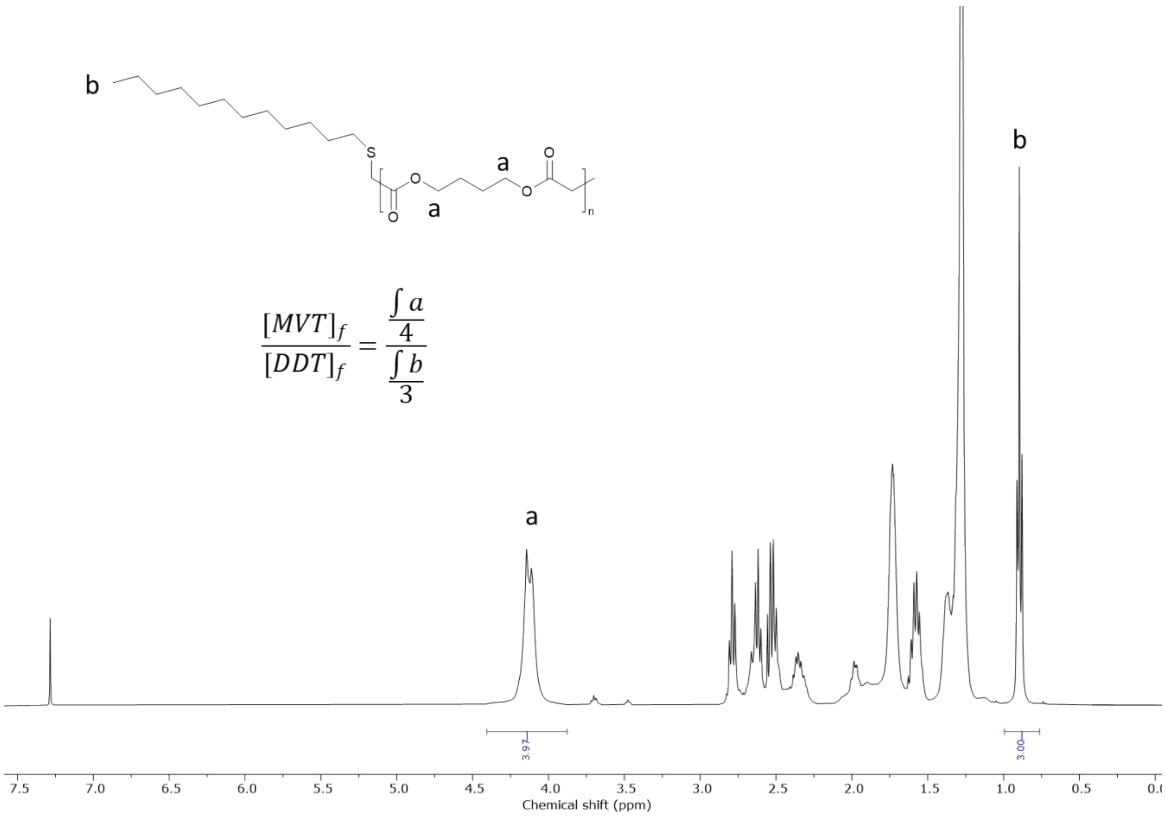
The linear telomerisations of BuA with DDT were performed according to the procedure above. BuA (4.00 g, 31.21 mmol, 2 equiv.), DDT (3.16 g, 15.60 mmol, 1 equiv.), AIBN (76.9 mg, 0.47 mmol, 1.5 mol% equiv.) and toluene (7.16 g, 77.69 mmol, 50 wt%) were utilised in the preparation of the stock solution.



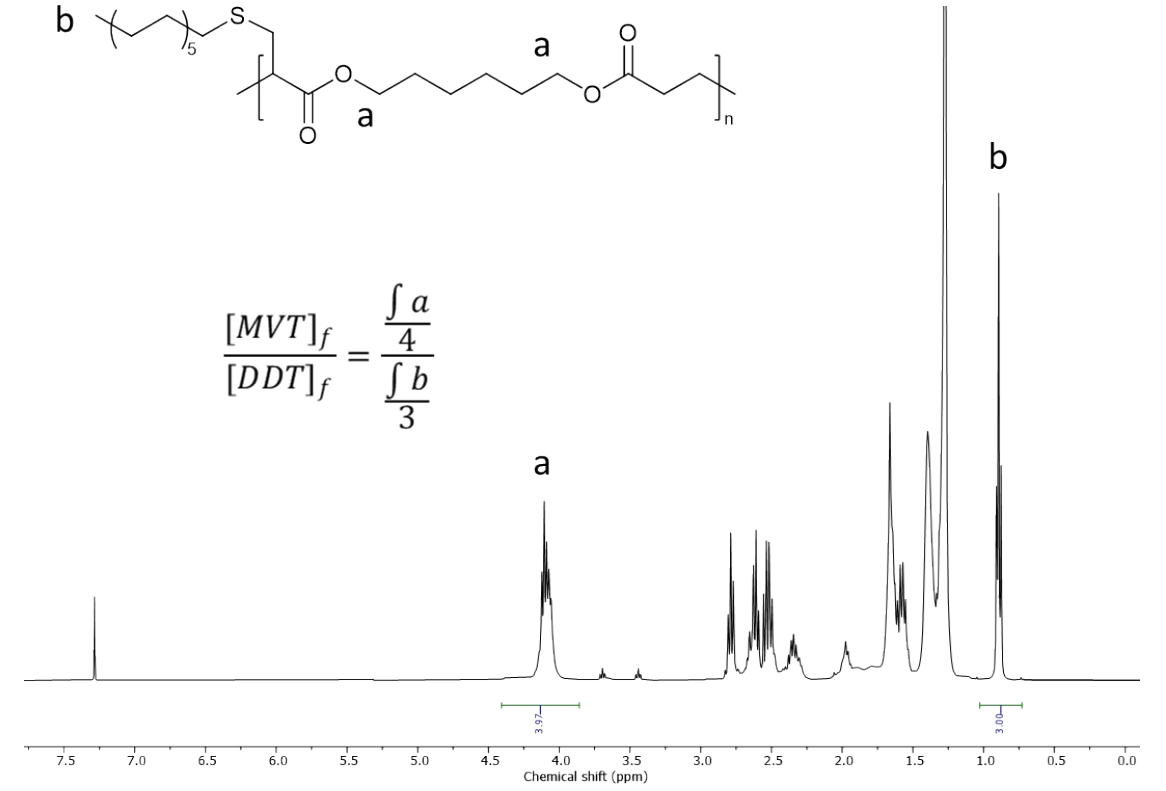
ESI Figure S1: ^{1}H NMR spectroscopic analysis demonstrating how to calculate the molar ratio of MVT (1,4 butanediol diacrylate) to telogen (DDT) at t = 0. $[MVT]_0/[DDT]_0$ demonstrated here = 0.5. This example is also applicable to 1,6 hexanediol diacrylate.



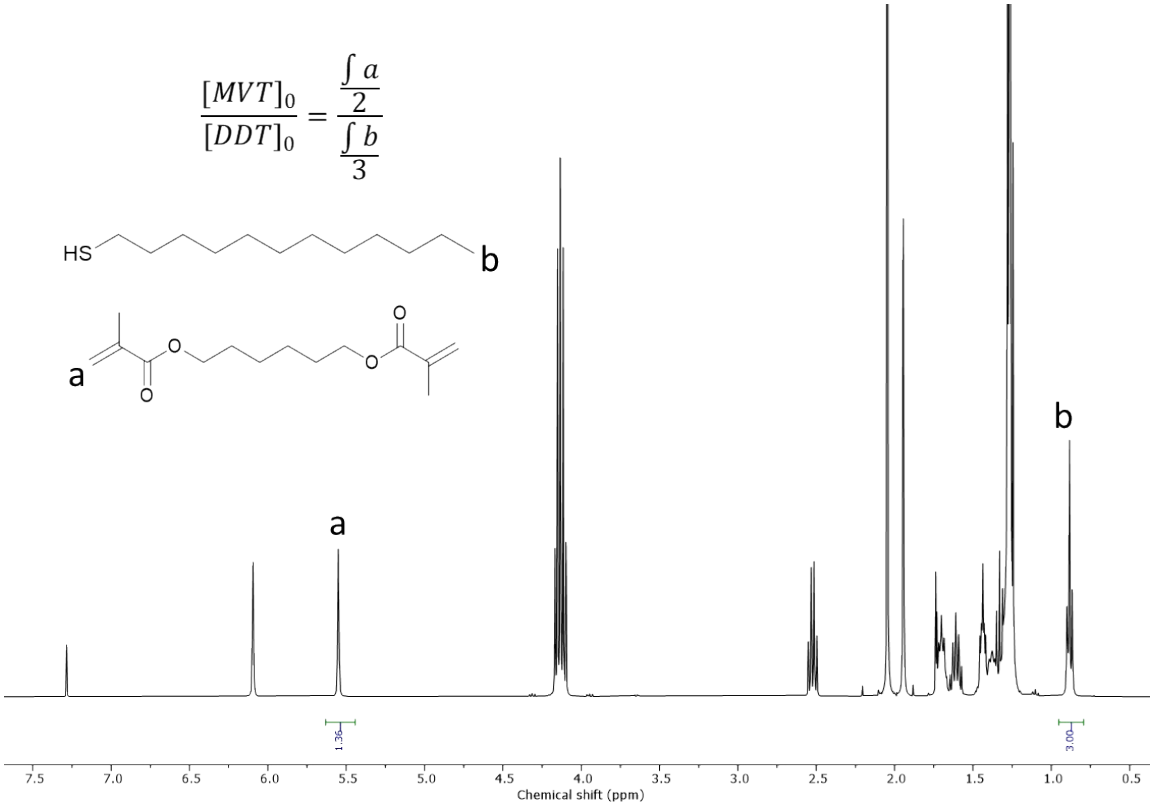
ESI Figure S2: ^{1}H NMR spectroscopic analysis of crude *p*(BDA-DDT) TBRT reaction mixture at t = 24 hours. Zoomed in region between 6.5 ppm and 5.5 ppm demonstrating disappearance of vinyl peaks which translates to > 99% vinyl conversion. This example is also applicable to 1,6 hexanediol diacrylate



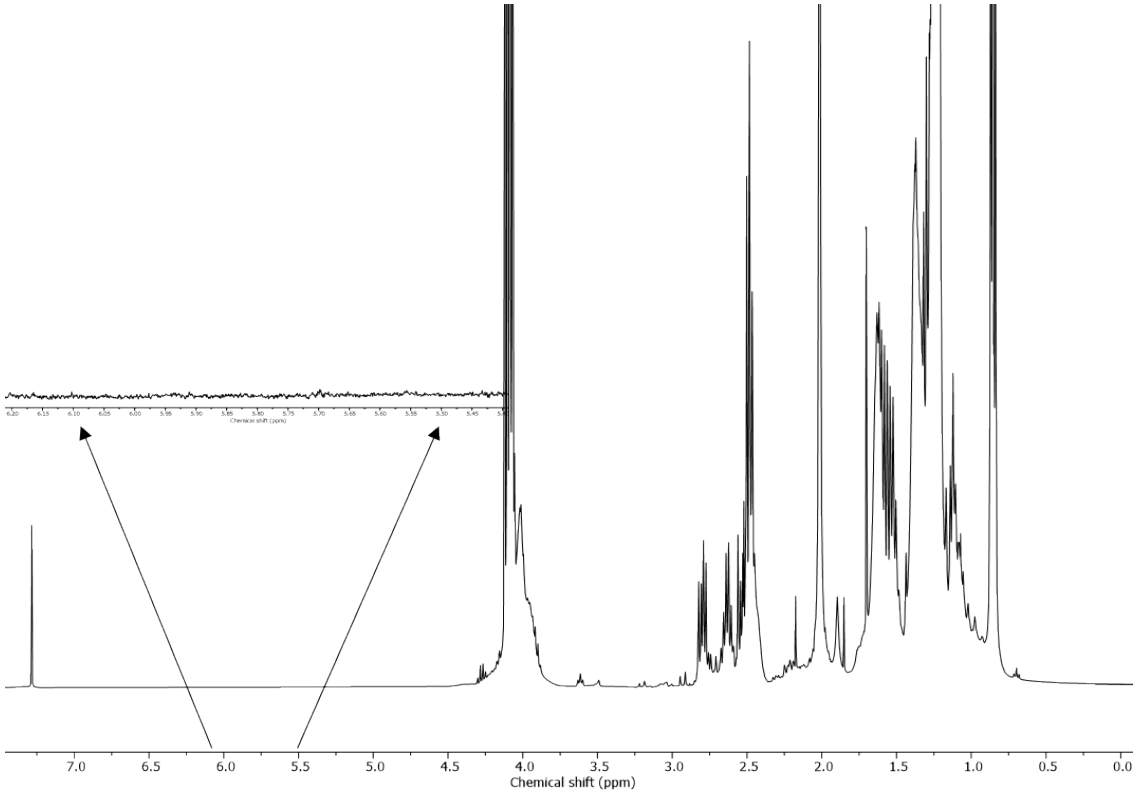
ESI Figure S3: ^{1}H NMR spectroscopic analysis demonstrating how to calculate final ratio of MVT (1,4 butanediol diacrylate) to telogen (DDT) within a purified polymer produced by TBRT.



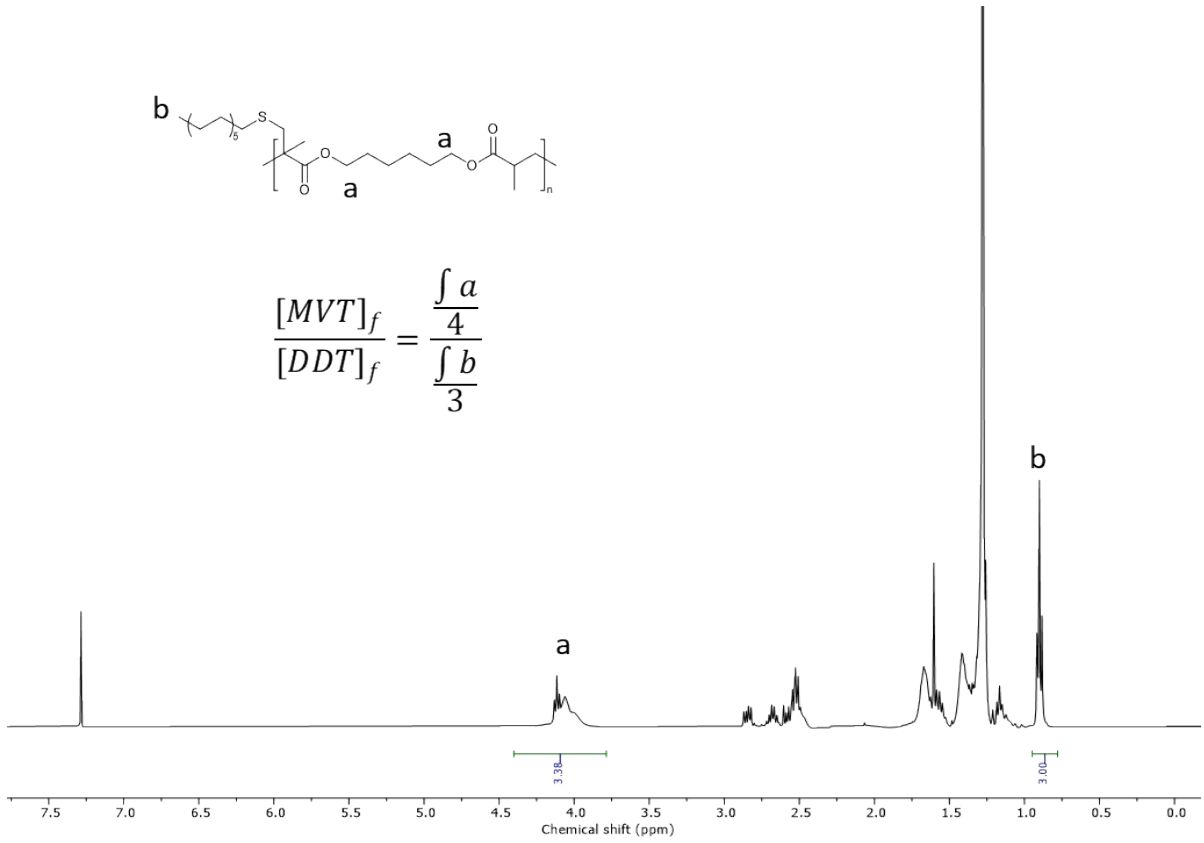
ESI Figure S4: ^{1}H NMR spectroscopic analysis demonstrating how to calculate final ratio of MVT (1,6 hexanediol diacrylate) to telogen (DDT) within a purified polymer produced by TBRT.



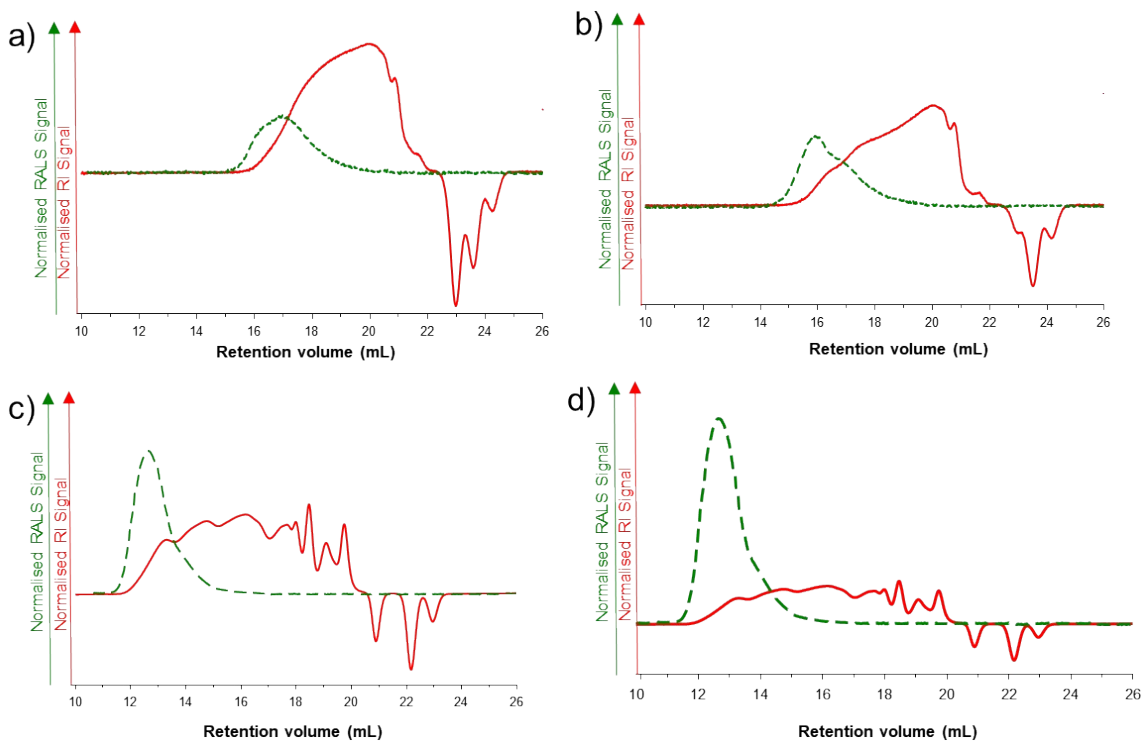
ESI Figure S5: ^{1}H NMR spectroscopic analysis demonstrating how to calculate the molar ratio of MVT (1,6 hexanediol dimethacrylate) to telogen (DDT) at t = 0. $[MVT]_0/[DDT]_0$ demonstrated here = 0.68. This example is also applicable to 1,4 butanediol dimethacrylate



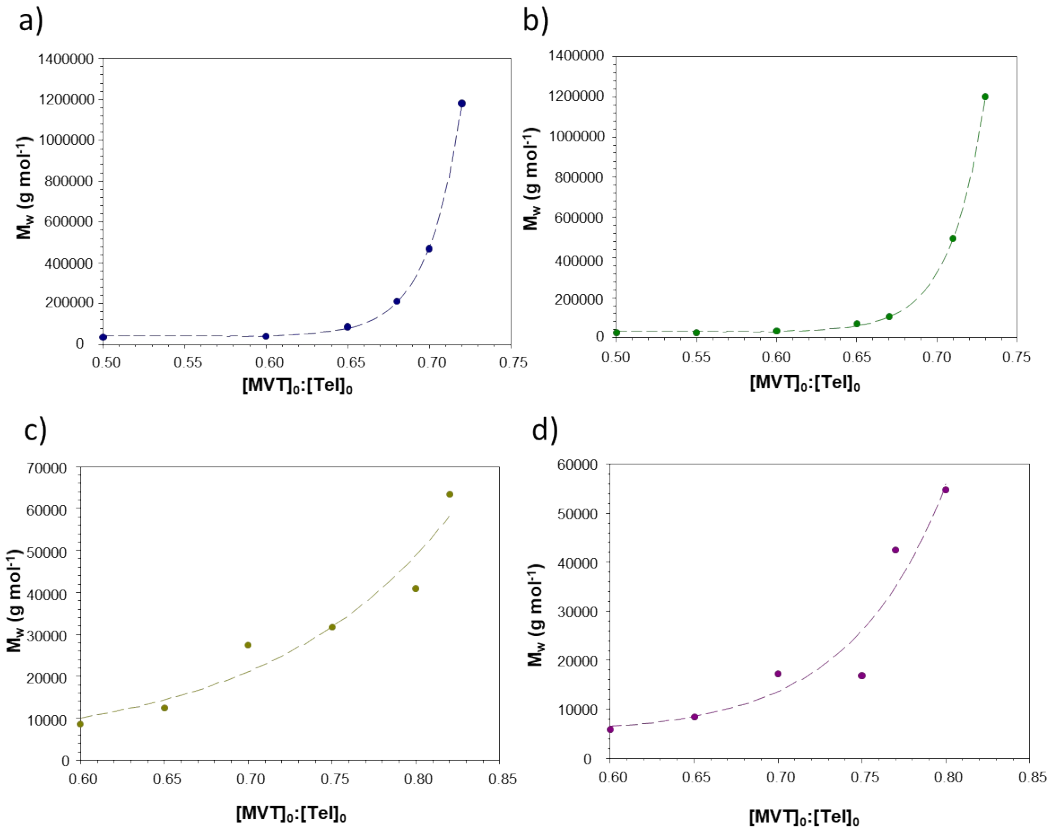
ESI Figure S6: ^{1}H NMR spectroscopic analysis of crude *p*(HDMA-DDT) TBRT reaction mixture at t = 24 hours. Zoomed in region between 6.2 ppm and 5.5 ppm demonstrating disappearance of vinyl peaks which translates to > 99 % vinyl conversion. This example is also applicable to 1,4 butanediol dimethacrylate.



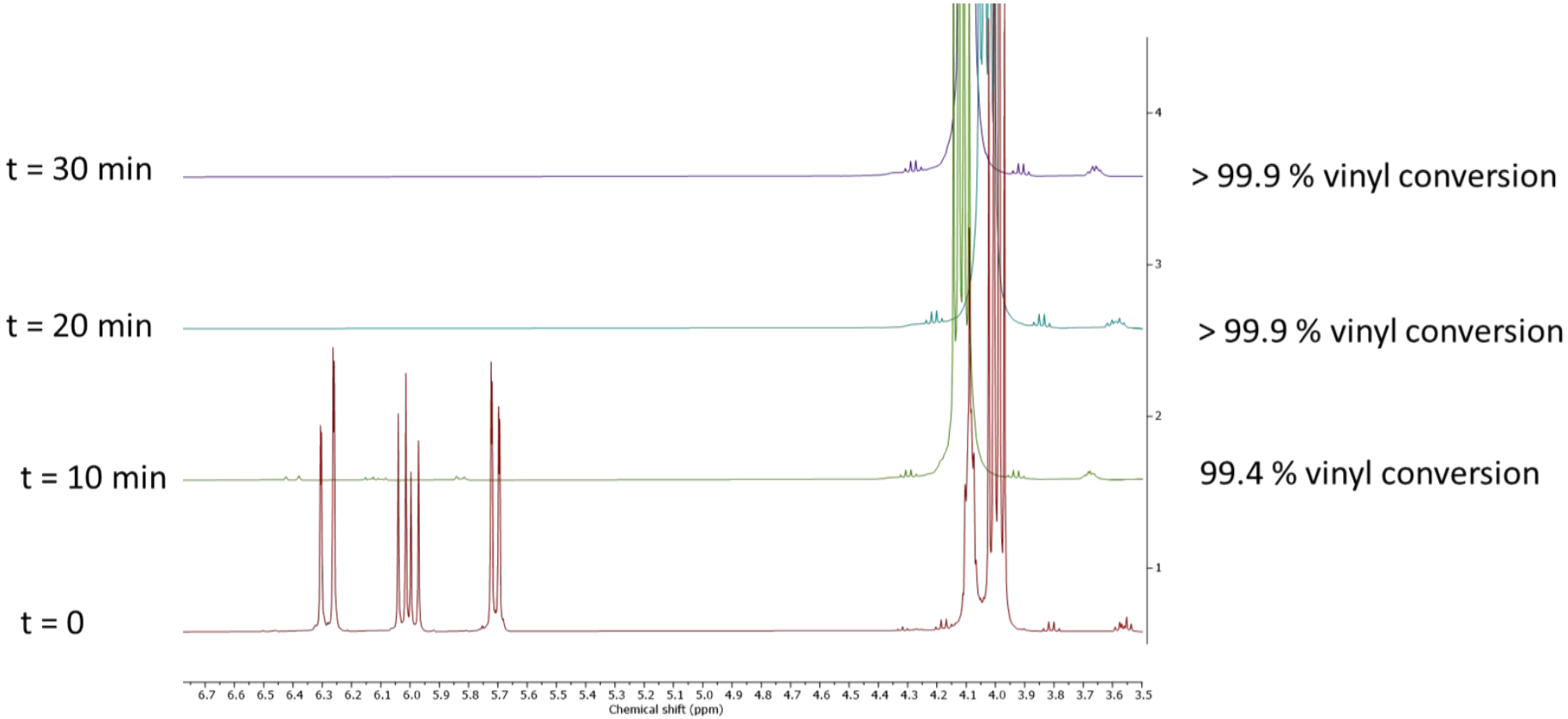
ESI Figure S7: ^{1}H NMR spectroscopic analysis demonstrating how to calculate final ratio of MVT (1,6 hexanediol dimethacrylate) to telogen (DDT) within a purified polymer produced by TBRT.



ESI Figure S8: Overlaid normalised RI (red solid line) and RALS (green dotted line) traces for a) p(DDT-BDDA), b) p(DDT-HDDA), c) p(DDT-BDMA) and d) p(DDT-HDMA) synthesised using $[MVT]_0/[Tel]_0$ initial feedstock ratios close to the gel point for each polymer. Each polymerisation was conducted at 70 °C.



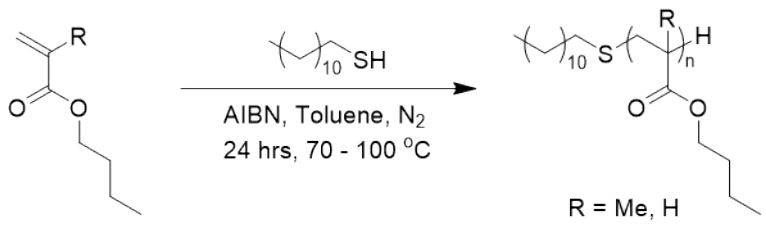
ESI Figure S9: Variation in M_w for the TBRT polymerisation reactions of a) BDMA, b) HDMA, c) BDA and d) HDA at varied $[MVT]_0/[Tel]_0$ ratios conducted at 70 °C using DDT as the telogen.



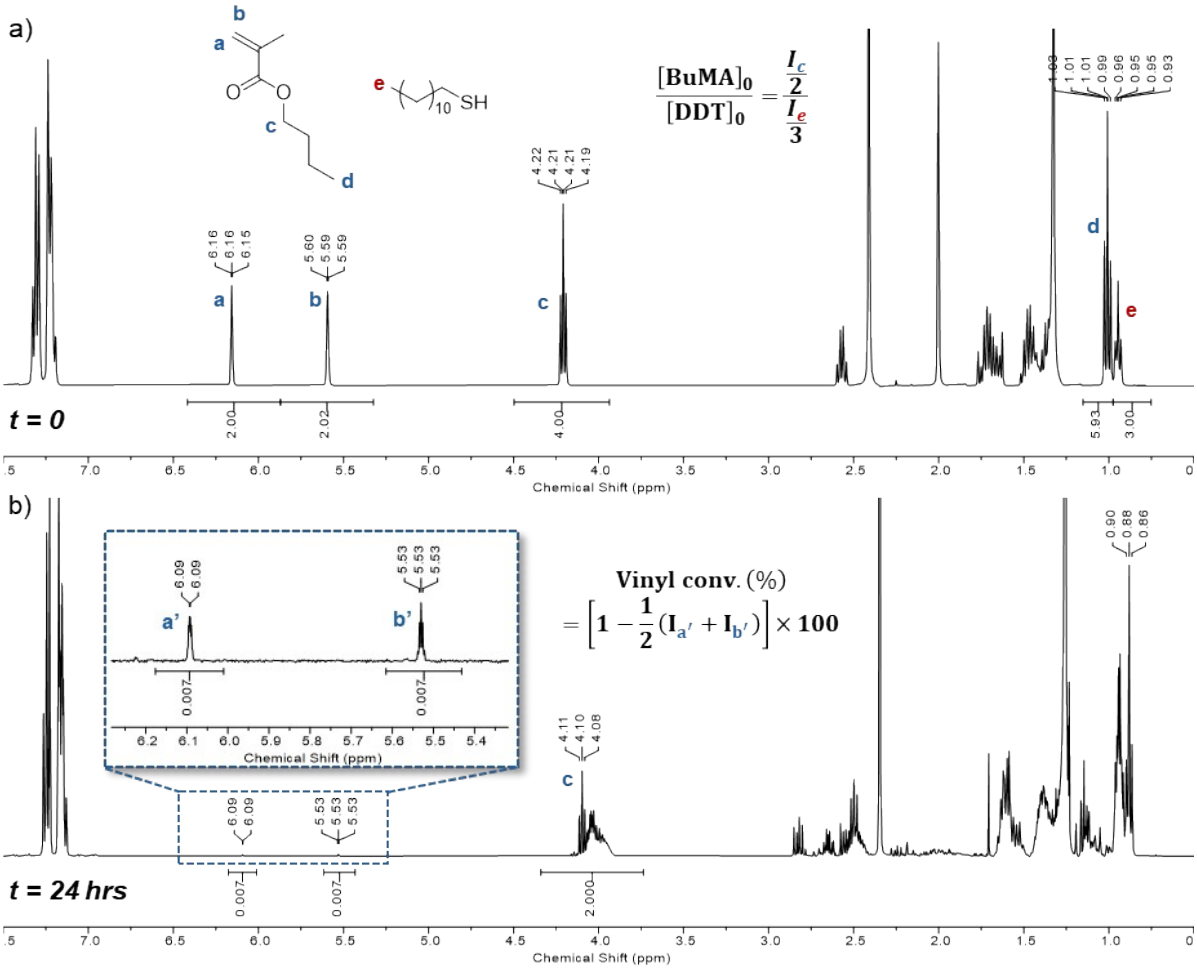
ESI Figure S10: ^{1}H NMR example spectra shown for determination of vinyl conversion during kinetic study of the TBRT of *p*(HDA-DDT). All values are referenced against initial analysis at t = 0.

Table S1: ^{1}H NMR spectroscopic kinetic analysis of the TBRT reactions of BDMA, HDMA, BDA and HDA at varied $[MVT]_0/[Tel]_0$ ratios conducted at 70 °C using DDT as the telogen.

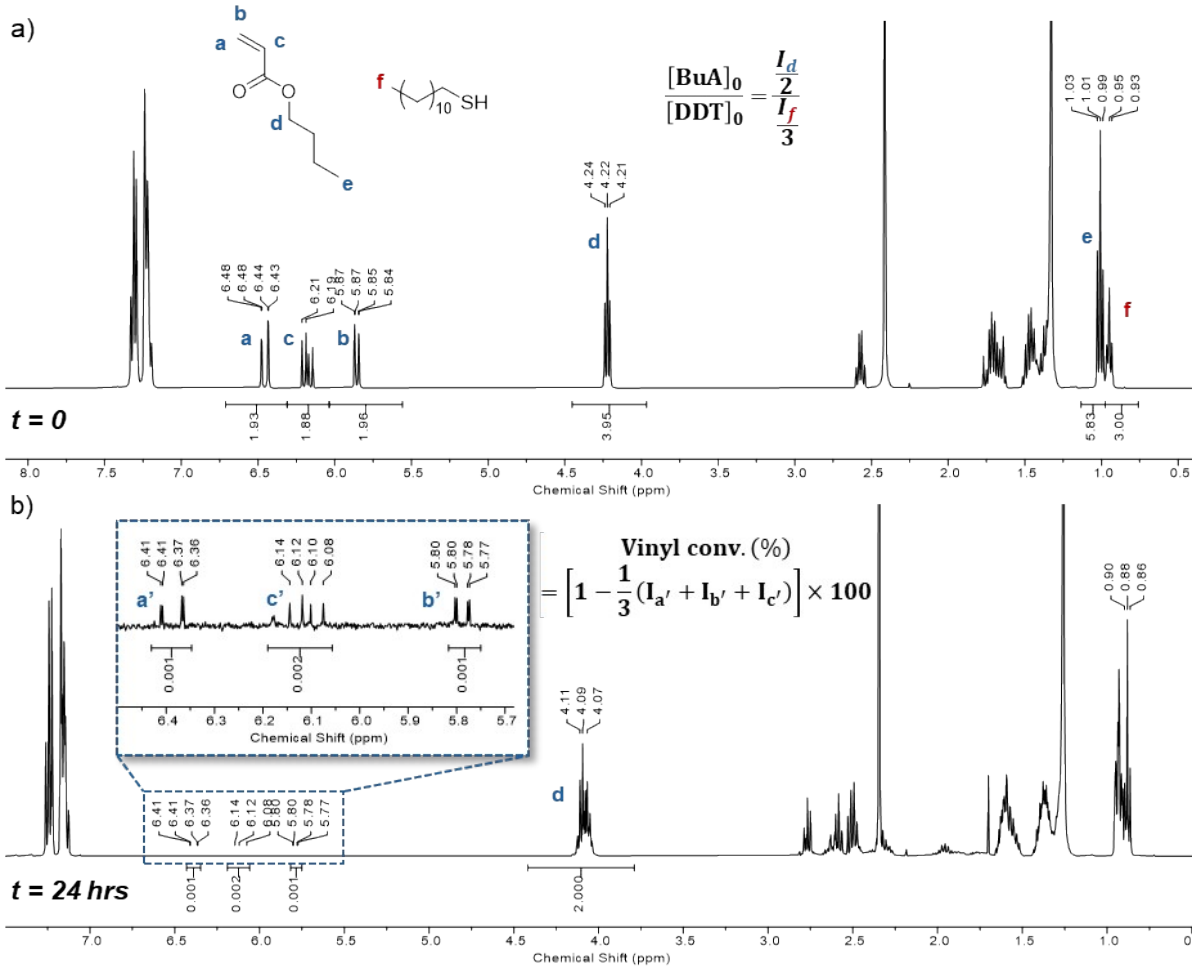
	^{1}H NMR ($CDCl_3$)			^{1}H NMR ($CDCl_3$)	
Taxogen	**Time (min)**	**Conversion (%)**	**Taxogen**	**Time (min)**	**Conversion (%)**
	0	0		0	0.0
	1	0.0		2	0.0
	2	2.8		4	10.4
	3	12.5		6	61.2
	4	30.6		8	91.0
BDA	5	59.7	HDA	10	92.5
	6	84.7		12	94.0
	7	97.2		14	99.8
	8	99.6		16	100.0
	9	100.0		18	100.0
	10	100.0		20	100.0
	0	0.0		0	0.0
	10	12.4		10	4.9
	20	34.6		20	20.9
	30	39.5		30	27.6
	40	49.2		40	43.8
	50	60.2		50	56.6
BDMA	60	66.3	HDMA	60	60.4
	75	81.3		75	72.9
	90	90.6		90	85.7
	105	92.5		105	89.0
	120	98.7		120	90.6
	150	100.0		150	95.6
	180	100.0		180	100.0



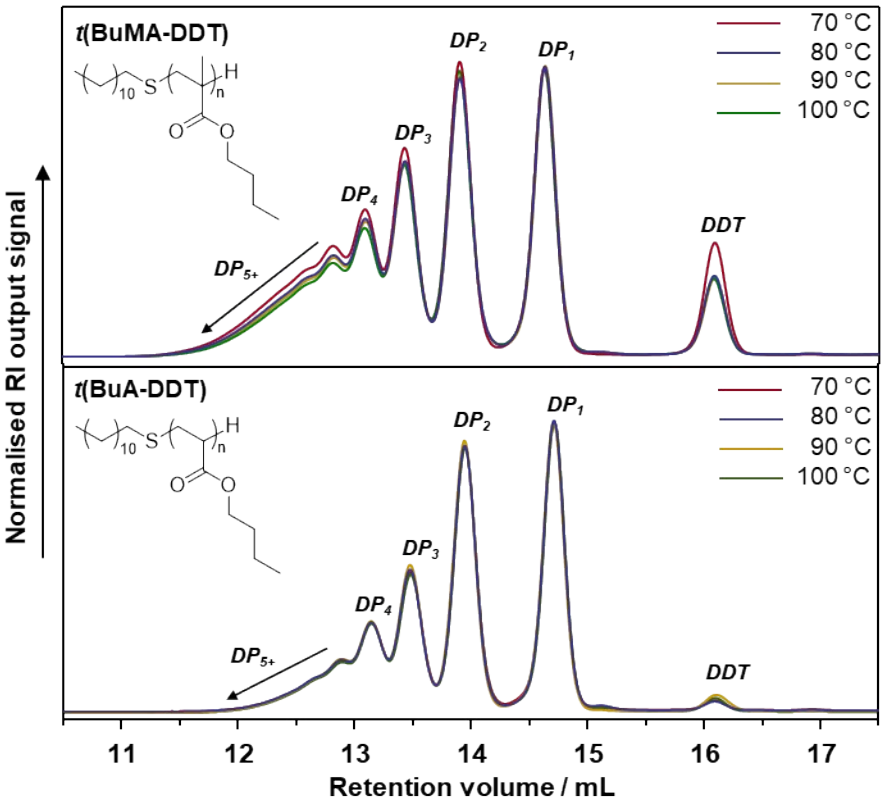
ESI Scheme S1: The synthesis of linear telomers of butyl methacrylate and butyl acrylate with DDT, conducted over a range of temperatures from 70 – 100 °C in toluene (50 wt%).



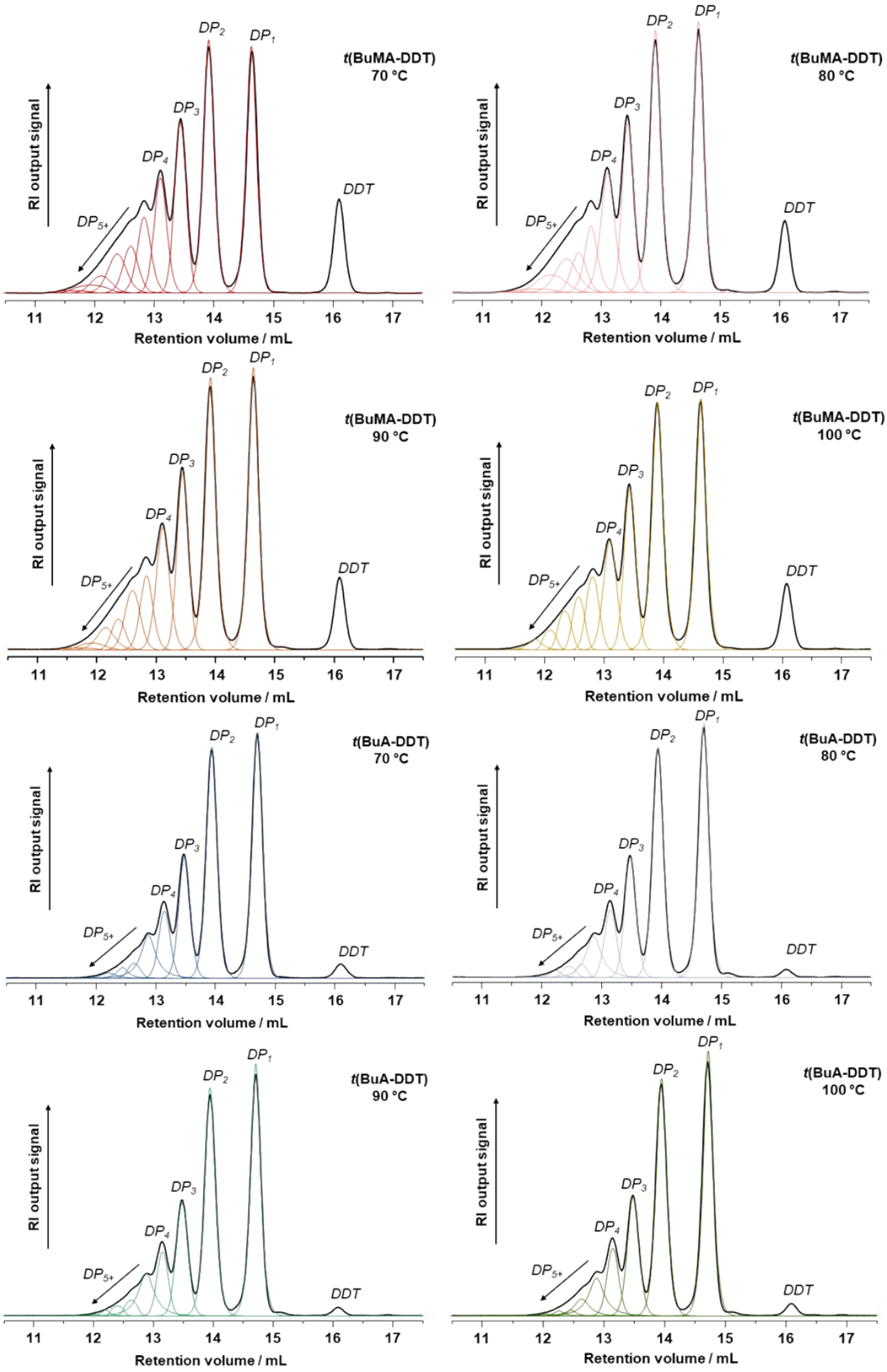
ESI Figure S11: Example ^{1}H NMR analysis for the linear telomerisation of BuMA with DDT. a) Analysis performed at t = 0, for the calculation of the feedstock ratio $[BuMA]_0/[DDT]_0$, provided the calibration of $I_e = 3$. b) Analysis performed after 24 hours of reaction, for the calculation of vinyl conversion using the calibration of $I_c = 2$.



ESI Figure S12: Example ^{1}H NMR analysis for the linear telomerisation of BuA with DDT. a) Analysis performed at t = 0, for the calculation of the feedstock ratio $[BuA]_0/[DDT]_{0'}$ provided the calibration of $I_f = 3$. b) Analysis performed after 24 hours of reaction, for the calculation of vinyl conversion using the calibration of $I_d = 2$.



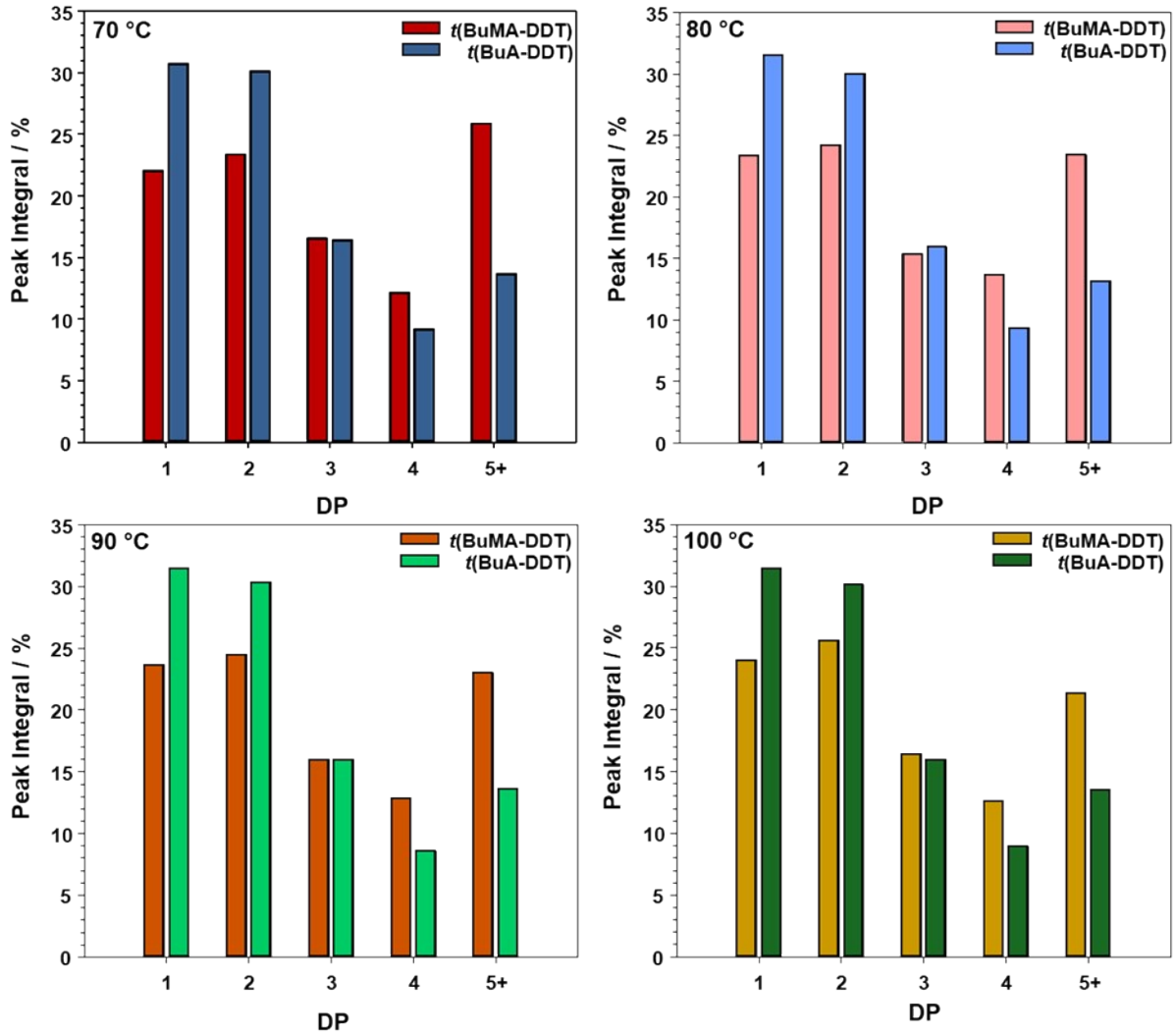
ESI Figure S13: Size exclusion chromatography analysis of linear telomers of BuMA and BuA with DDT generated at varying temperatures of 70 – 100 °C. Telomer residues with defined *DP* values are annotated, and those with reduced resolution combined as DP_{5+}. Traces have been normalised to the height of the DP_1 signal.



ESI Figure S14: Deconvolution processing of SEC analysis of *t*(BuMA-DDT) and *t*(BuA-DDT) telomers generated at varying temperatures of 70 – 100 °C. Peak fitting was performed using a Gauss-Loren cross function with statistical weighting. Telomer residues with defined *DP* values are annotated, and those with reduced resolution combined as DP_{5+}. Traces have been normalised to the height of the DP_1 signal.

ESI Table S2: Analysis detailing the peak integrals of each resolved peak (DP_x) of linear telomer distributions of *t*(BuMA-DDT) and *t*(BuA-DDT). Signals corresponding to DP ≥ 5 have been combined due to decreasing resolution.

		Peak Integral (%)				
Composition	**Temperature (°C)**	DP_1	DP_2	DP_3	DP_4	DP_{5+}
***t*(BuMA-DDT)**	70	22.1	23.4	16.6	12.1	25.9
	80	23.3	24.3	15.3	13.7	23.4
	90	23.7	24.5	16.0	12.9	23.0
	100	24.0	25.6	16.4	12.6	21.3
***t*(BuA-DDT)**	70	30.7	30.1	16.4	9.1	13.7
	80	31.5	30.0	15.9	9.3	13.2
	90	31.5	30.3	16.0	8.6	13.6
	100	31.5	30.1	16.0	8.9	13.5



ESI Figure S15: Peak integral comparison from SEC deconvolution processing for *t*(BuMA-DDT) and *t*(BuA-DDT) telomers generated at varying temperatures of 70 – 100 °C.