Electronic Supplementary Material (ESI) for Polymer Chemistry.

Impact of multi-vinyl taxogen dimensions on high molecular weight soluble polymer synthesis using Transfer-dominated Branching Radical Telomerisation

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Supplementary Information:

Experimental

Materials

Ethylene glycol dimethacrylate (EGDMA, 98%) was purchased from Alfa Aesar. 1,6-hexanediol dimethacrylate (HDMA, 100 ppm MeHQ, >98%) and 1,12-dodecanediol dimethacrylate (LDMA, 100 ppm MeHQ, >95%) were purchased from TCI Chemicals. Methyl methacrylate (MMA, <30 ppm MeHQ, 99%), Hexyl methacrylate (HMA, 100 ppm MeHQ, 98%), 1-dodecanethiol (DDT, >98%), 2,2'-Azobis(2-methylpropionitrile) (AIBN, 98%), deuterated chloroform (CDCl3, 99.8 atom% D) and aluminium oxide (activated, basic, Brockmann I) were purchased from Sigma Aldrich. Lauryl methacrylate (LMA, 500 ppm MeHQ, 96%), was purchased from Sigma Aldrich and was generally used as received (for kinetic experiments, the MeHQ was removed using a basic alumina column). Ethyl Acetate (EtOAc, analytical grade), Tetrahydrofuran (THF, HPLC-grade) and Methanol (MeOH, analytical grade 99.9%) 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 ($CDCl_3$) 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 a Malvern Viscotek instrument, equipped with a GPC_{max} VE2001 auto-sampler, two Viscotek T6000M columns (and a guard column) and a triple detector array TDA305 containing a refractive index (RI) detector VE3580 and a 270 Dual Detector (light scattering and viscometer). A mobile phase of THF containing 2 v/v % of triethylamine at 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 (Viscotek, M_w = 105 kg/mol, Đ = 1.022 and M_w = 245 kg/mol, Đ = 2.272 respectively) were used as calibrants. All TD-SEC analysis of linear telomers was performed using a Malvern Viscotek instrument, equipped with a GPC_{max} VE2001 auto-sampler, a mixed column setup of one T2000 column and one T1000 column in series (and a guard column) and a triple detector array TDA302 containing a refractive index (RI) detector VE3580 and a 270 Dual Detector (light scattering and viscometer). A mobile phase of THF at 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 poly(methyl methacrylate) standards (Viscotek, M_w = 1010 g/mol, Đ = 1.14 and M_w = 1760 g/mol, Đ = 1.15 respectively) were used as calibrants. All TD-SEC associated data were estimated using Omnisec 4.7 software. Matrix-assisted laser desorption ionisation – time of flight (MALDI-TOF) mass spectra of linear telomers were analysed using a Bruker Autoflex Mass Spectrometer (Materials Innovation Factory, Liverpool, UK). Spectra for samples containing MMA, HMA and LMA were each the sum of 500 shots acquired in positive-reflectron mode. Cesium triiodide (CsI_3) and α-cyano-4-hyrdroxycinnamic acid (HCCA) were used as the mass scale calibrant and matrix, respectively. Both the matrix and samples were prepared at 10 mg/mL in THF. The solutions were combined at a 5:1 v/v ratio of matrix to sample. 2 µL of the prepared solutions were deposited onto stainless-steel sample plates and air dried prior to analysis. 3D branched polymer structures were modelled using Spartan 18 software.

Example TBRT of MVT with varying equivalents of DDT

In a typical TBRT experiment using EGDMA at a targeted $[MVT]_0/[DDT]_0$ ratio of 0.85, EGDMA (1.98 g, 10.00 mmol, 0.85 equiv.), DDT (2.38 g, 11.76 mmol, 1 equiv.), AIBN (49.3 mg, 0.30 mmol) and EtOAc (4.50 g, 51.07 mmol) were loaded into a 25 mL round-bottomed flask equipped with a magnetic stirrer bar. 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 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, affording typically a white precipitate and cloudy dispersion. The precipitate was washed further with fresh methanol (3 x 50 mL) and subsequently dried in vacuo overnight at 40 °C. Finally, a sample of the purified polymer was taken for ^{1}H NMR and TD-SEC analysis.

Using HDMA, a TBRT experiment targeting a $[MVT]_0/[DDT]_0$ ratio of 0.70 would require HDMA (2.54 g, 10.00 mmol, 0.70 equiv.), DDT (2.89 g, 14.29 mmol, 1 equiv.), AIBN (49.3 mg, 0.30 mmol) and EtOAc (4.50 g, 51.07 mmol). Using LDMA, a TBRT experiment targeting a $[MVT]_0/[DDT]_0$ ratio of 0.55 would require LDMA (3.38 g, 10.00 mmol, 0.55 equiv.), DDT (3.68 g, 18.18 mmol, 1 equiv.), AIBN (49.3 mg, 0.30 mmol) and EtOAc (4.50 g, 51.07 mmol).

Preliminary TBRT experiments for EGDMA and LDMA utilised MVT (1.00 g, X < 1 equiv.), DDT (1 equiv.) AIBN (1.5 mol% *versus* vinyl bonds) and EtOAc (50 wt% *versus* MVT + DDT) under the same experimental conditions and using the same procedure as stated above.

General procedure for TBRT kinetic experiments

In a typical TBRT kinetic experiment using EGDMA at a targeted $[MVT]_0/[DDT]_0$ ratio of 0.85, EGDMA (15.86 g, 80.00 mmol, 0.85 equiv.), DDT (19.05 g, 94.12 mmol, 1 equiv.), AIBN (0.39 g, 2.40 mmol) and EtOAc (35.00 g, 0.40 mol) were loaded into a dual-necked 250 mL round-bottomed flask equipped with a magnetic stirrer bar. 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 45 minutes using a nitrogen purge. The flask was then heated to 70 °C with stirring and allowed to proceed under a nitrogen atmosphere. Samples were extracted at regular time intervals and vinyl conversions were estimated by ^{1}H NMR spectroscopy. Crude samples were either concentrated in vacuo or diluted with THF (< 5 mL), depending on their viscosity, to obtain suitable viscosity for precipitation. All crude samples were then precipitated into cold methanol. Purified samples were dried in vacuo under an air vortex and finally air dried for 24 hours. Samples incapable of precipitation were concentrated in vacuo using a spiral evaporator and analysed without further purification. All samples were then analysed using TD-SEC.

A TBRT kinetic experiment using HDMA, targeting a $[MVT]_0/[DDT]_0$ ratio of 0.70, required HDMA (20.35 g, 80.00 mmol, 0.70 equiv.), DDT (23.13 g, 114.29 mmol, 1 equiv.), AIBN (0.39 g, 2.40 mmol) and EtOAc (35.00 g, 0.40 mol). A TBRT kinetic experiment using LDMA, targeting a $[MVT]_0/[DDT]_0$ ratio of 0.55, required LDMA (27.08 g, 80.00 mmol, 0.55 equiv.), DDT (29.44 g, 145.45 mmol, 1 equiv.), AIBN (0.39 g, 2.40 mmol) and EtOAc (35.00 g, 0.40 mol).

General procedure for FRP kinetic experiments

In a typical FRP kinetic experiment using MMA, MMA (5.00 g, 49.94 mmol, 1 equiv.), AIBN (0.12 g, 0.75 mmol, 1.5 mol% equiv.) and EtOAc (5.00 g, 56.75 mmol, 50 wt% *versus* monomer) were loaded into a 25 mL round-bottomed flask equipped with a magnetic stirrer bar. The solution was homogenised by agitation and a sample was extracted for ^{1}H NMR spectroscopic analysis of the reaction mixture prior to initiation. The solution was deoxygenated whilst stirring for 30 minutes using a nitrogen purge. The solution was then heated to 70 °C under magnetic stirring and allowed to proceed under a nitrogen atmosphere. Samples were

extracted and exposed to air at regular time intervals and vinyl conversions were estimated by ^{1}H NMR spectroscopy. Crude samples were concentrated in vacuo using a spiral evaporator and finally air dried for 24 hours. All samples were then analysed using TD-SEC.

An FRP kinetic experiment using HMA required HMA (5.00 g, 29.37 mmol, 1 equiv.), AIBN (0.07 g, 0.44 mmol, 1.5 mol% equiv.) and EtOAc (5.00 g, 56.75 mmol, 50 wt% *versus* monomer). An FRP kinetic experiment using LMA required LMA (5.00 g, 19.65 mmol, 1 equiv.), AIBN (0.05 g, 0.29 mmol, 1.5 mol% equiv.) and EtOAc (5.00 g, 56.75 mmol, 50 wt% *versus* monomer).

Determination of C_T *via* construction of Mayo plots

In a typical Mayo experiment using MMA at a targeted $[M]_0$:$[DDT]_0$ ratio of 100:1, MMA (2.00 g, 20.00 mmol, 100 equiv.), DDT (40.5 mg, 0.20 mmol, 1 equiv.), AIBN (49.3 mg, 0.30 mmol, 1.5 mol% equiv.) and EtOAc (2.04 g, 23.19 mmol, 50 wt% *versus* monomer + DDT) were loaded into a 10 mL round-bottomed flask equipped with a magnetic stirrer bar. For each monomer, a series of 6 reactions were conducted using $[M]_0$:$[DDT]_0$ feedstock ratios of approximately 1:0, 100:1, 150:1, 200:1, 250:1 and 300:1. 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 flask was then heated to 70 °C under magnetic stirring. The polymerisation was stopped prematurely (< 10% vinyl conversion) *via* exposure to air and rapid cooling in an ice bath. Reactions containing MMA, HMA and LMA were terminated at 15 minutes, 6 minutes and between 5 and 10 minutes respectively, in accordance with time points pertaining to approximately 5% vinyl conversion as determined during control FRP kinetic experiments. A sample was then taken from the reaction for estimation of monomer conversion by ^{1}H NMR spectroscopy. The crude samples were concentrated *via* evaporation and precipitated into cold methanol. The samples were dried in vacuo using a spiral evaporator and finally air dried for 24 hours. The purified samples were then analysed using TD-SEC.

Using HMA, a Mayo experiment targeting a $[M]_0$:$[DDT]_0$ ratio of 100:1 would require HMA (3.41 g, 20.00 mmol, 100 equiv.), DDT (40.5 mg, 0.20 mmol, 1 equiv.), AIBN (49.3 mg, 0.30 mmol, 1.5 mol% equiv.) and EtOAc (3.45 g, 39.10 mmol, 50 wt% *versus* monomer + DDT). Using LMA, a Mayo experiment targeting a $[M]_0$:$[DDT]_0$ ratio of 100:1 would require LMA

(5.09 g, 20.00 mmol, 100 equiv.), DDT (40.5 mg, 0.20 mmol, 1 equiv.), AIBN (49.3 mg, 0.30 mmol, 1.5 mol% equiv.) and EtOAc (5.13 g, 58.21 mmol, 50 wt% *versus* monomer + DDT).

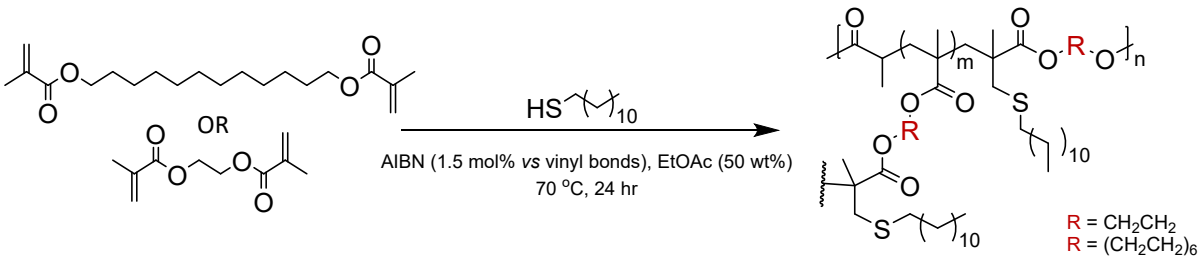
General procedure for linear telomerisations

In a typical linear telomerisation using MMA, MMA (4.00 g, 40.00 mmol, 2 equiv.), DDT (4.05 g, 20.00 mmol, 1 equiv.), AIBN (98.5 mg, 0.60 mmol, 1.5 mol% equiv.) and EtOAc (8.00 g, 90.80 mmol) were loaded into a 25 mL round-bottomed flask equipped with a magnetic stirrer bar. The solution was homogenised by agitation and a sample was extracted for ^{1}H NMR spectroscopic analysis of the reaction mixture prior to initiation. The solution was deoxygenated whilst stirring for 30 minutes using a nitrogen purge. The solution was then heated to 70 °C 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 crude samples were concentrated in vacuo initially using a spiral evaporator and finally a vacuum oven at 40 °C for 24 hours. All samples were then analysed using TD-SEC.

A linear telomerisation using HMA required HMA (6.81 g, 40.00 mmol, 2 equiv.), DDT (4.05 g, 20.00 mmol, 1 equiv.), AIBN (98.5 mg, 0.60 mmol, 1.5 mol% equiv.) and EtOAc (8.00 g, 90.80 mmol). A linear telomerisation using LMA required LMA (10.18 g, 40.00 mmol, 2 equiv.), DDT (4.05 g, 20.00 mmol, 1 equiv.), AIBN (98.5 mg, 0.60 mmol, 1.5 mol% equiv.) and EtOAc (8.00 g, 90.80 mmol).

General procedure for solvent fractionation experiments

In a typical solvent fractionation, a sample of polymer (*p*($DDT_{1.00}$-$EGDMA_{0.85}$), *p*($DDT_{1.00}$-$HDMA_{0.70}$) or *p*($DDT_{1.00}$-$LDMA_{0.54}$)) was dissolved in the minimum volume of tetrahydrofuran in a beaker equipped with a magnetic stirrer bar. An ice bath was placed under the beaker and methanol was added slowly to the stirring solution until the solution became slightly turbid. The liquid was allowed to settle, typically revealing a biphasic separation consisting of a turbid upper layer and clear, viscous lower layer. The upper layer was removed by pipetting and the polymer isolated in vacuo by rotary evaporation and finally in a vacuum oven at 40 °C for 24 hours. The lower layer was air dried and finally dried in a vacuum oven at 40 °C for 24 hours. All samples were then analysed using TD-SEC and ^{1}H NMR spectroscopy.



Scheme S1. Synthesis of branched polymers *via* the TBRT of EGDMA and LDMA with DDT at 50 wt% solids content.

Table T1. ^{1}H NMR spectroscopic and TD-SEC analysis of branched polymers generated *via* the TBRT of EGDMA and LDMA with DDT at 50 wt% solids content.

		^{1}H NMR ($CDCl_3$)			TD-SEC (THF/TEA) [d]				
Entry	MVT	$[MVT]_0/[DDT]_0$ [a]	Conv (%) [b]	$[MVT]_f/[DDT]_f$ [c]	M_w (g mol^{-1})	M_n (g mol^{-1})	Đ	α	dn/dc
1	EGDMA	0.90	Gel	Gel	-	-	-	-	-
2	EGDMA	0.88	Microgel [e]	Microgel	-	-	-	-	-
3	EGDMA	0.85	> 99	1.00	1 208 000	13 631	88.64	0.337	0.0941
4	EGDMA	0.81	> 99	1.03	304 250	4 517	67.35	0.313	0.0929
5	EGDMA	0.76	> 99	1.00	119 657	1 836	65.14	0.318	0.0925
6	EGDMA	0.70	> 99	0.96	60 854	2 879	21.14	0.297	0.0924
7	LDMA	0.79	Gel	Gel	-	-	-	-	-
8	LDMA	0.70	Gel	Gel	-	-	-	-	-
9	LDMA	0.64	Gel	Gel	-	-	-	-	-
10	LDMA	0.60	> 99	0.95	799 734	16 764	47.70	0.444	0.0860
11	LDMA	0.54	> 99	0.89	63 372	2 780	22.79	0.357	0.0831
12	LDMA	0.49	> 99	0.85	20 595	1 954	10.54	0.319	0.0818

[a] Determined for sample analysed at t = 0. See example equation in Figure S1. [b] Determined for crude sample analysed at t = 24 hr, referenced against sample analysed at t = 0. See example in Figure S2. [c] Determined for sample analysed after purification and drying *in vacuo*. See example equation in Figure S3. [d] Determined by TD-SEC using a 2% v/v TEA/THF eluent system. [e] Sample gave strong resistance to filtration through a 0.2 µm PTFE syringe filter despite appearing homogenous during TBRT.

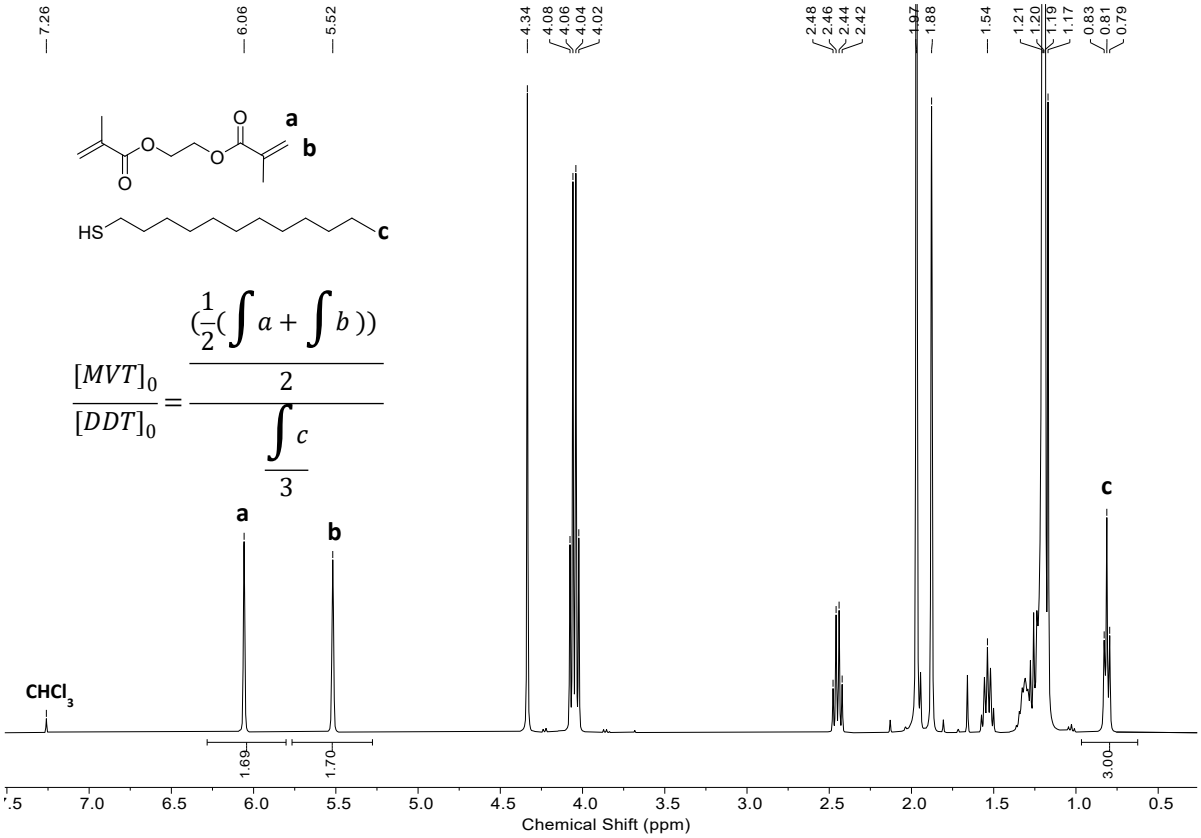


Figure S1. Table T1 entry 3, ^{1}H NMR spectroscopic analysis at t = 0 for calculation of $[MVT]_0/[DDT]_0$.

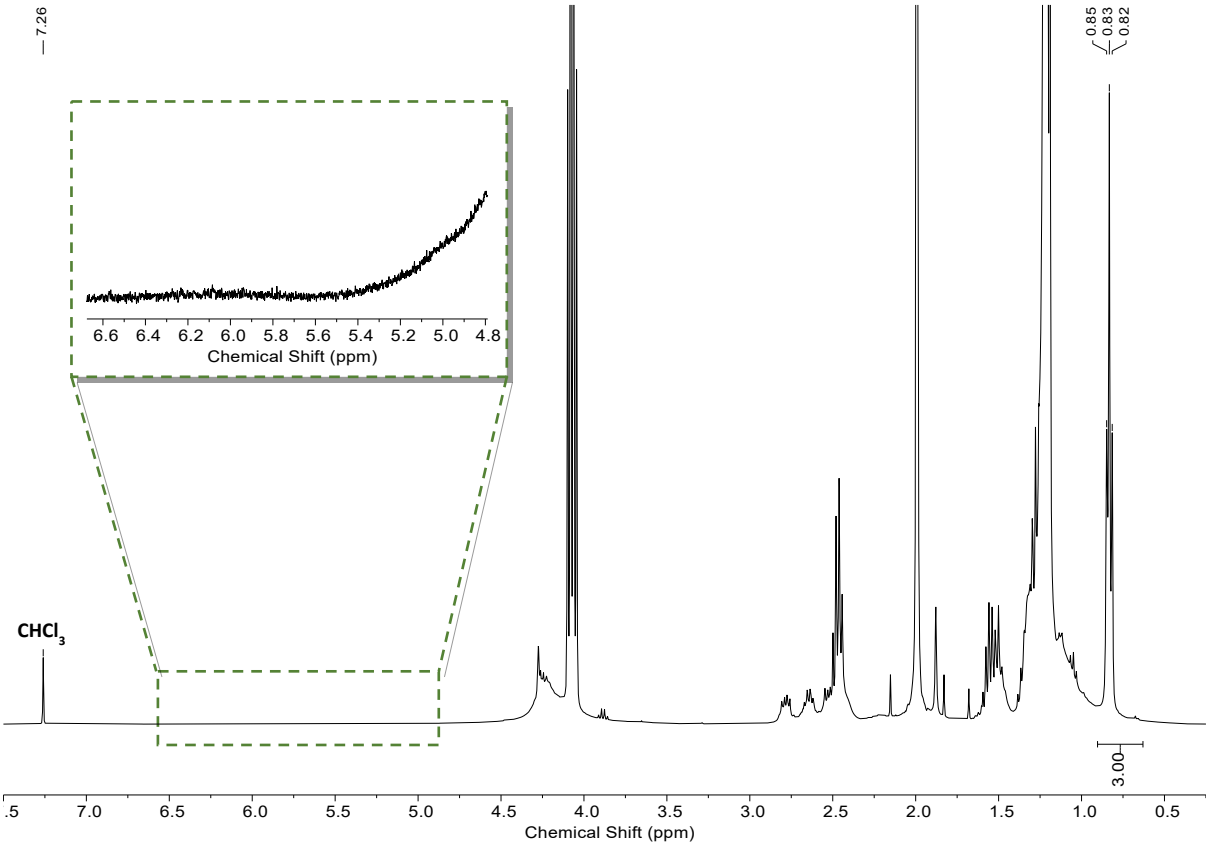


Figure S2. Table T1 entry 3, ^{1}H NMR spectroscopic analysis of crude sample at t = 24 hours, showing disappearance of vinyl bonds. In all tables, this outcome has been assigned a vinyl conversion >99%.

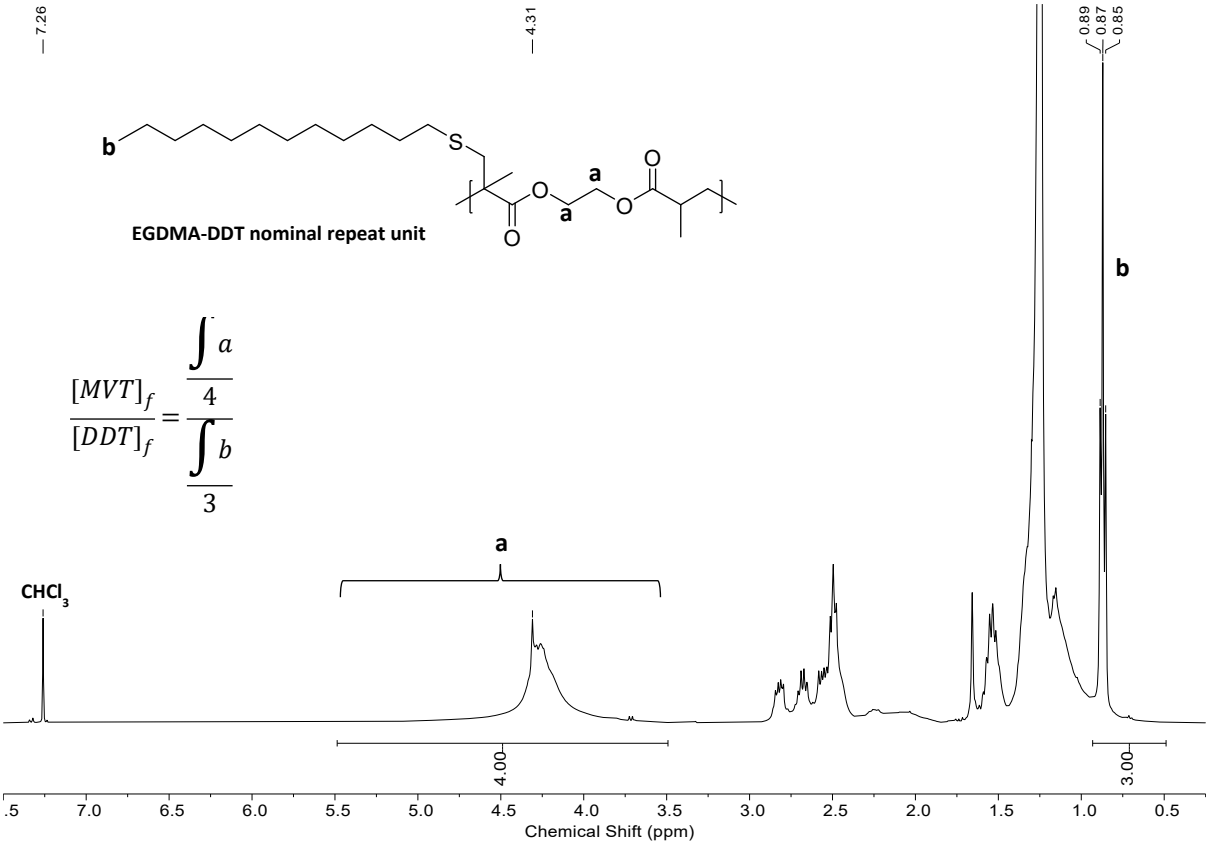


Figure S3. Table S1 entry 3, ^{1}H NMR spectroscopic analysis of purified and dried polymer for calculation of $[MVT]_f/[DDT]_f$.

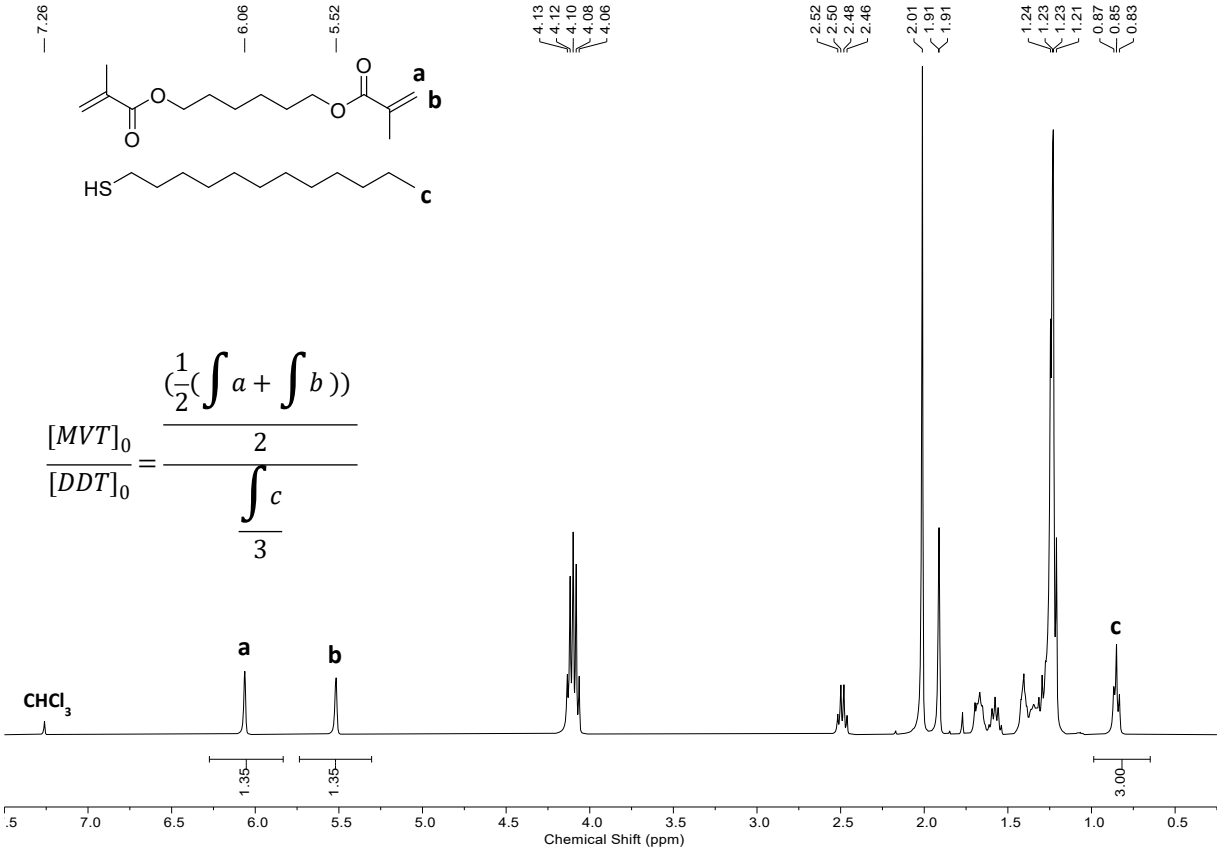


Figure S4. Table 1 entry 13, ^{1}H NMR spectroscopic analysis at t = 0 for calculation of $[MVT]_0/[DDT]_0$.

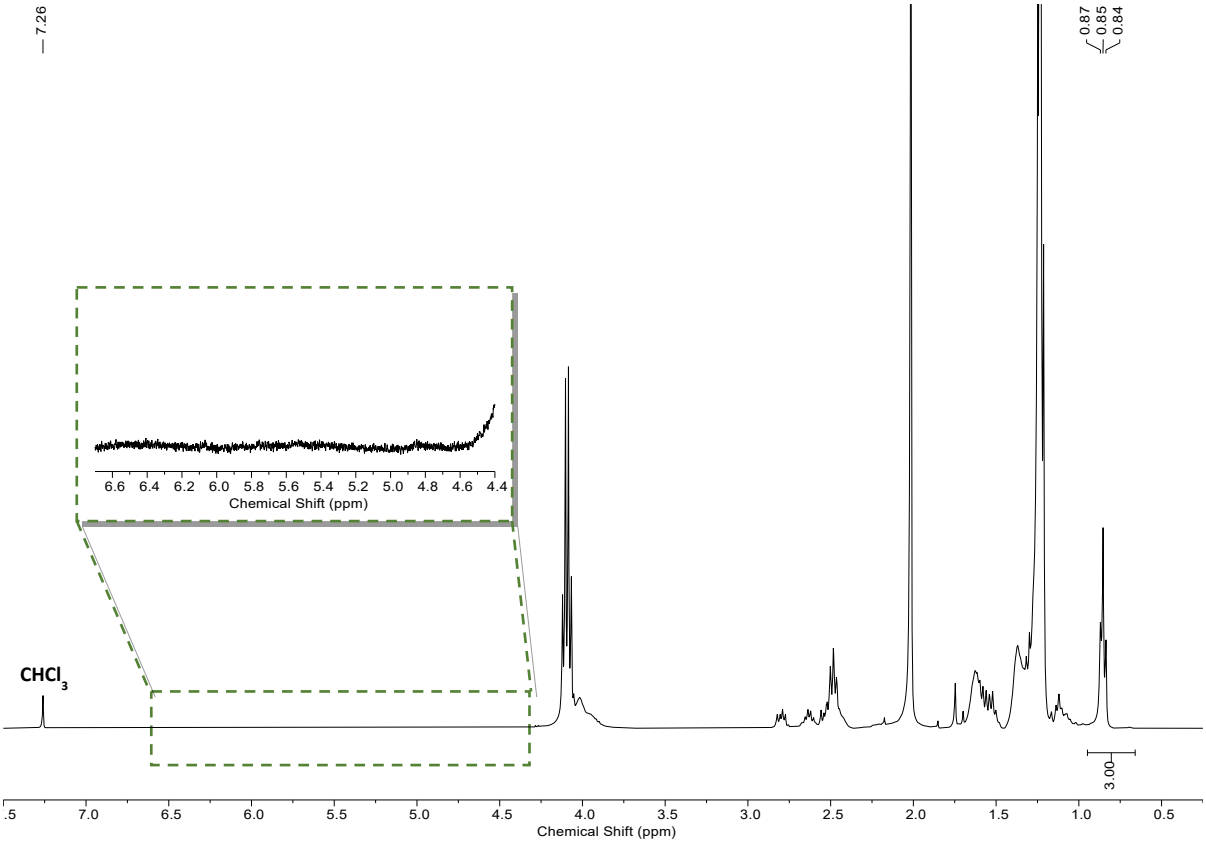


Figure S5. Table 1 entry 13, ^{1}H NMR spectroscopic analysis of crude sample at t = 24 hours, showing disappearance of vinyl bonds. In all tables, this outcome has been assigned a vinyl conversion >99%.

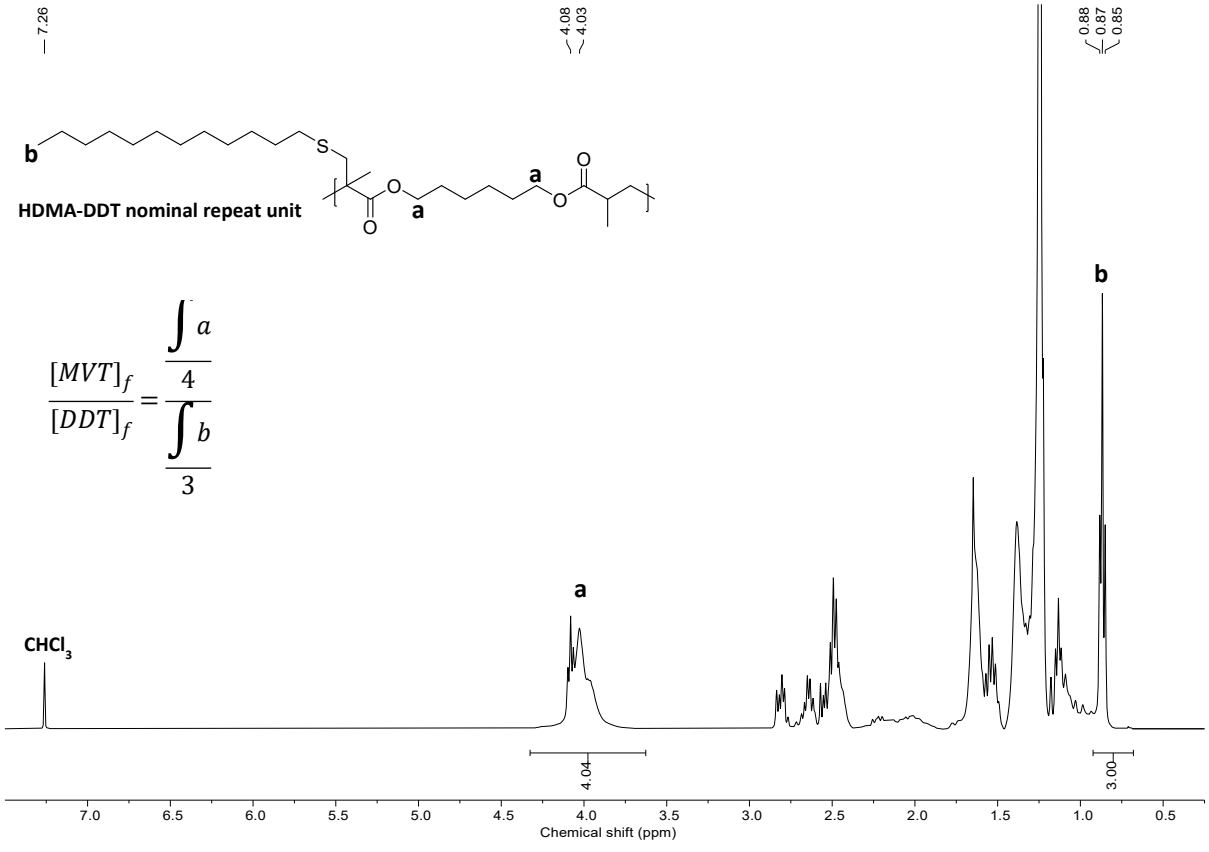


Figure S6. Table 1 entry 13, ^{1}H NMR spectroscopic analysis of purified and dried polymer for calculation of $[MVT]_f/[DDT]_f$.

Table T2. ^{1}H NMR spectroscopic and TD-SEC analyses of kinetics experiments using monofunctional monomers MMA, HMA and LMA by conventional free radical polymerisation.

		^{1}H NMR ($CDCl_3$)	TD-SEC (THF/TEA) [b]				
Mon	Time (min)	Conv (%) [a]	M_w (g mol^{-1})	M_n (g mol^{-1})	Đ	α	dn/dc [c]
MMA	0	0					
	5	0					
	10	1					
	15	5					
	20	9					
	25	12	TD-SEC data not obtained for MMA kinetic experiment				
	30	16					
	40	22					
	50	28					
	60	34					
	90	49					
	120	61					
	150	75					
HMA	0	0	-	-	-	-	-
	5	5	6 943	4 630	1.50	0.757	0.0736
	10	12	16 128	9 990	1.61	0.742	0.0736
	15	19	24 660	13 752	1.79	0.752	0.0736
	20	24	31 903	17 024	1.87	0.728	0.0736
	25	29	38 104	20 755	1.84	0.723	0.0736
	30	33	44 001	23 243	1.89	0.709	0.0736
	40	42	56 009	30 244	1.85	0.727	0.0736
	50	49	66 385	35 286	1.88	0.718	0.0736
	60	56	72 895	38 054	1.92	0.708	0.0736
	90	73	90 228	46 882	1.93	0.722	0.0736
	120	83	117 491	62 231	1.89	0.703	0.0736
LMA	0	0	-	-	-	-	-
	5	5	11 680	5 033	2.32	0.756	0.0753
	10	11	28 384	14 724	1.93	0.724	0.0753
	15	18	45 333	24 608	1.84	0.700	0.0753
	20	23	56 188	29 712	1.89	0.703	0.0753
	25	27	65 596	32 864	1.99	0.710	0.0753
	30	32	76 631	39 086	1.96	0.708	0.0753
	40	42	90 468	46 746	1.94	0.708	0.0753
	50	48	104 739	51 820	2.02	0.703	0.0753
	60	54	120 970	60 944	1.99	0.700	0.0753
	90	70	154 920	79 327	1.96	0.703	0.0753
	120	81	176 767	84 876	2.08	0.695	0.0753
	180	94	210 309	103 143	2.04	0.687	0.0753

[a] Determined for samples taken at specified intervals referenced against sample analysed at t = 0. See Figure S7. [b] Determined by TD-SEC using a 2% v/v TEA/THF eluent system. [c] Average dn/dc values were obtained over six injections for each of purified linear *p*(HMA) and *p*(LMA) samples of M_n = 14 283 g mol^{-1} and M_n = 18 001 g mol^{-1}, respectively.

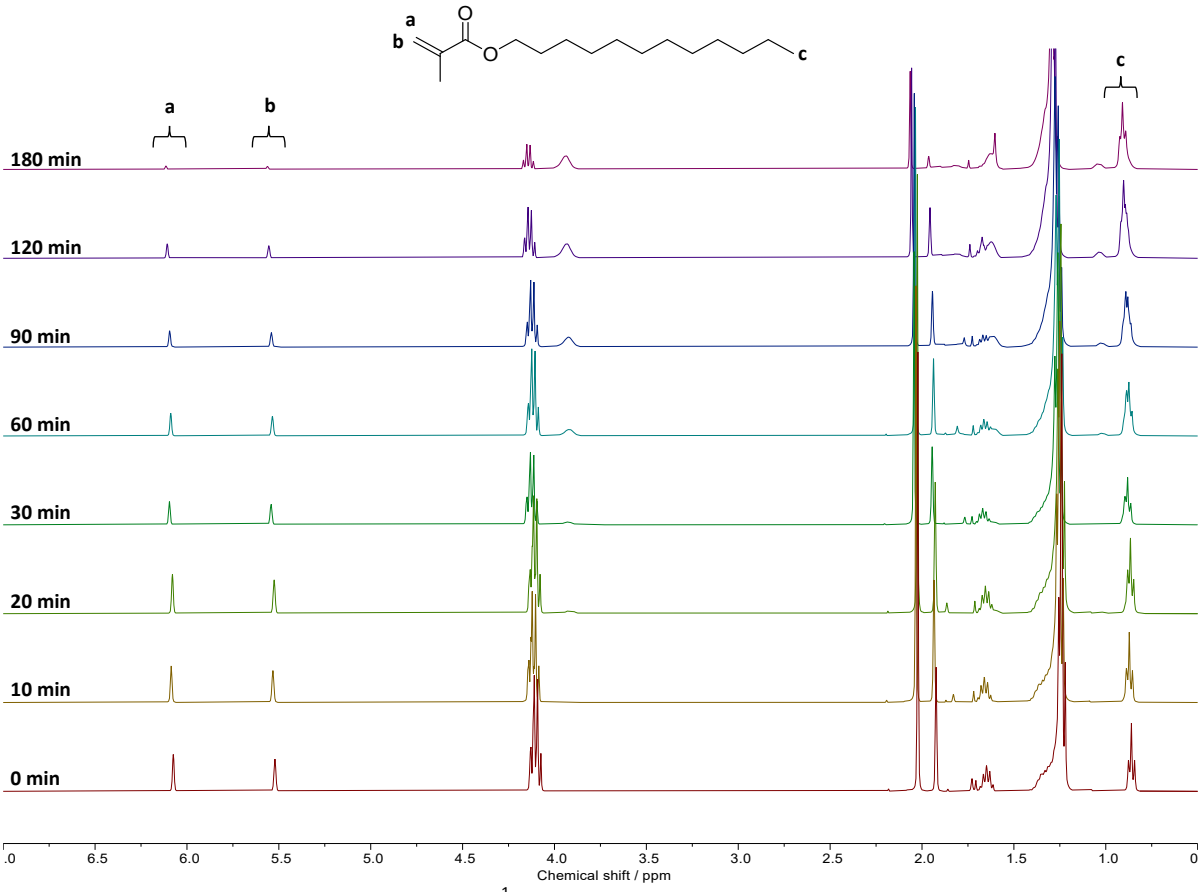


Figure S7. Table T2 LMA series, selection of ^{1}H NMR spectra shown for the monitoring of vinyl conversion during the kinetic study of LMA by FRP. All vinyl conversions are referenced against analysis taken at t = 0.

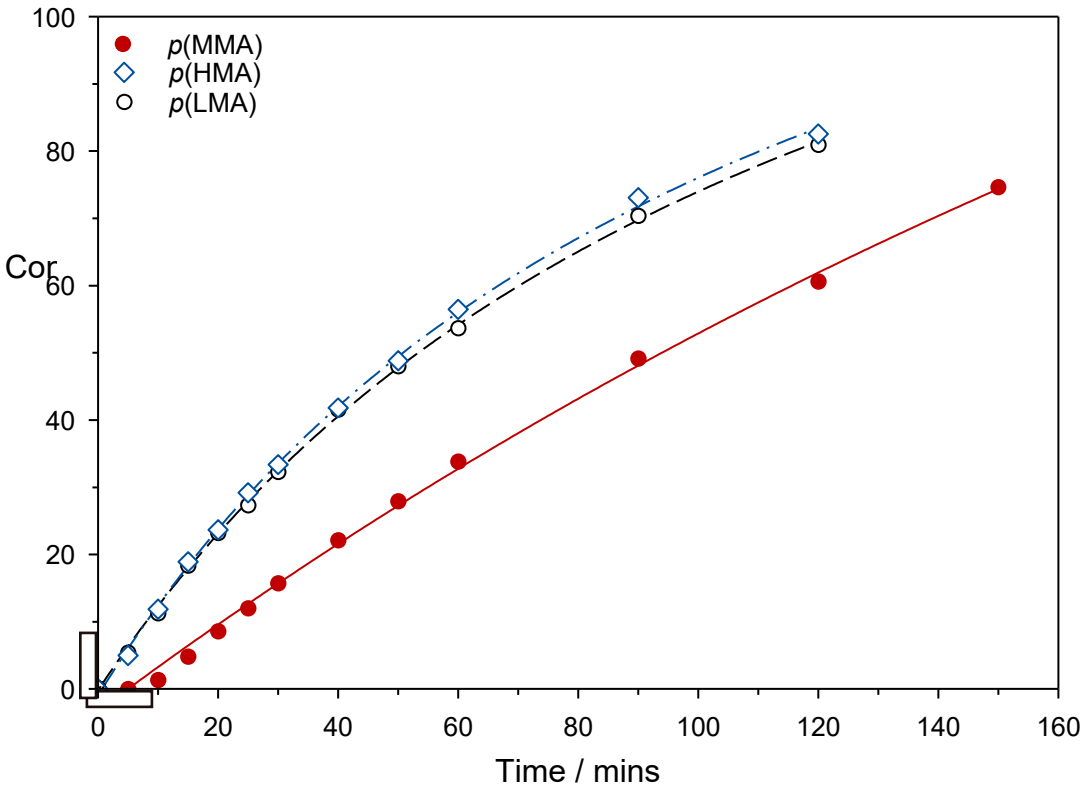


Figure S8. Comparison of vinyl conversion evolution for linear *p*(MMA), *p*(HMA) and *p*(LMA) during FRP kinetic experiments.

Table T3. ^{1}H NMR spectroscopic and TD-SEC analyses of kinetics experiments of $p(DDT_{1.00}\text{-}EGDMA_{0.85})$, $p(DDT_{1.00}\text{-}HDMA_{0.70})$ and $p(DDT_{1.00}\text{-}LDMA_{0.54})$ by TBRT.

		^{1}H NMR ($CDCl_3$)	TD-SEC (THF/TEA) [b]					
$[MVT]_0/[DDT]_0$	Time (hr)	Conv (%) [a]	M_w (g mol^{-1})	M_n (g mol^{-1})	Đ	α	dn/dc	R_H (nm)
$[EGDMA]_{0.85}/[DDT]_{1.00}$	0	0	-	-	-	-	-	-
	0.16	0	is	is	is	is	is	is
	0.33	5	is	is	is	is	is	is
	0.50	12	is	is	is	is	is	is
	0.66	18	is	is	is	is	is	is
	0.83	25	is	is	is	is	is	is
	1.00	32	7 476	3 024	2.47	0.255	0.0939	1.71
	1.25	43	11 577	2 838	4.08	0.298	0.0849	1.91
	1.50	55	15 981	3 611	4.43	0.105	0.0910	2.03
	1.75	64	24 271	3 424	7.09	0.232	0.0889	2.37
	2.00	72	38 973	4 523	8.62	0.287	0.0854	2.94
	2.50	84	147 549	4 210	35.04	0.313	0.0801	4.59
	3.00	94	732 598	11 859	61.77	0.335	0.0738	7.33
	4.00	> 99	1 611 000	11 484	140.28	0.341	0.0845	11.15
	5.00	> 99	1 906 000	11 678	163.21	0.369	0.0727	11.37
$[HDMA]_{0.70}/[DDT]_{1.00}$	0	0	-	-	-	-	-	-
	0.25	12	is	is	is	is	is	is
	0.50 [c]	23	1 605	716	2.24	0.227	0.0600	0.73
	0.75 [c]	32	2 788	2 105	1.32	0.284	0.0607	0.99
	1.00	43	6 309	3 388	1.86	0.274	0.0757	1.59
	1.25	52	9 746	3 133	3.11	0.279	0.0730	1.76
	1.50	62	11 448	3 661	3.13	0.296	0.0724	1.90
	1.75	69	14 970	3 468	4.32	0.309	0.0737	2.11
	2.00	76	22 924	3 507	6.54	0.317	0.0715	2.41
	2.50	87	71 012	4 186	16.96	0.341	0.0714	3.61
	3.00	96	332 422	4 939	67.30	0.356	0.0725	6.31
	4.00	> 99	655 362	6 851	95.66	0.361	0.0701	8.02
	5.00	> 99	652 607	6 459	101.04	0.362	0.0702	7.99
$[LDMA]_{0.54}/[DDT]_{1.00}$	0	0	-	-	-	-	-	-
	0.16	5	is	is	is	is	is	is
	0.33	16	is	is	is	is	is	is
	0.50	30	is	is	is	is	is	is
	0.66	41	is	is	is	is	is	is
	0.83 [c]	52	13 183	6 106	2.16	0.336	0.0377	1.74
	1.00 [c]	61	13 767	4 206	3.35	0.360	0.0442	1.80
	1.25	73	19 205	3 237	5.93	0.349	0.0726	2.50
	1.50	83	47 000	3 655	12.86	0.357	0.0719	3.39
	1.75	91	136 010	4 083	33.31	0.360	0.0746	4.90
	2.00	97	340 820	4 411	77.26	0.366	0.0757	6.78
	2.50	> 99	380 030	4 098	93.69	0.366	0.0762	7.10
	3.00	> 99	386 095	4 974	77.62	0.360	0.0763	7.20
	4.00	> 99	387 558	5 308	73.01	0.368	0.0757	7.17
	5.00	> 99	390 147	4 695	83.08	0.368	0.0777	7.17

[a] Determined for samples taken at specified intervals referenced against sample analysed at t = 0. [b] Determined by TD-SEC using a 2% v/v TEA/THF eluent system. [c] TD-SEC samples analysed as crudes (could not be precipitated) at 25 mg/mL to boost light scattering. is = "insufficient scattering" for determination of molecular weight data.

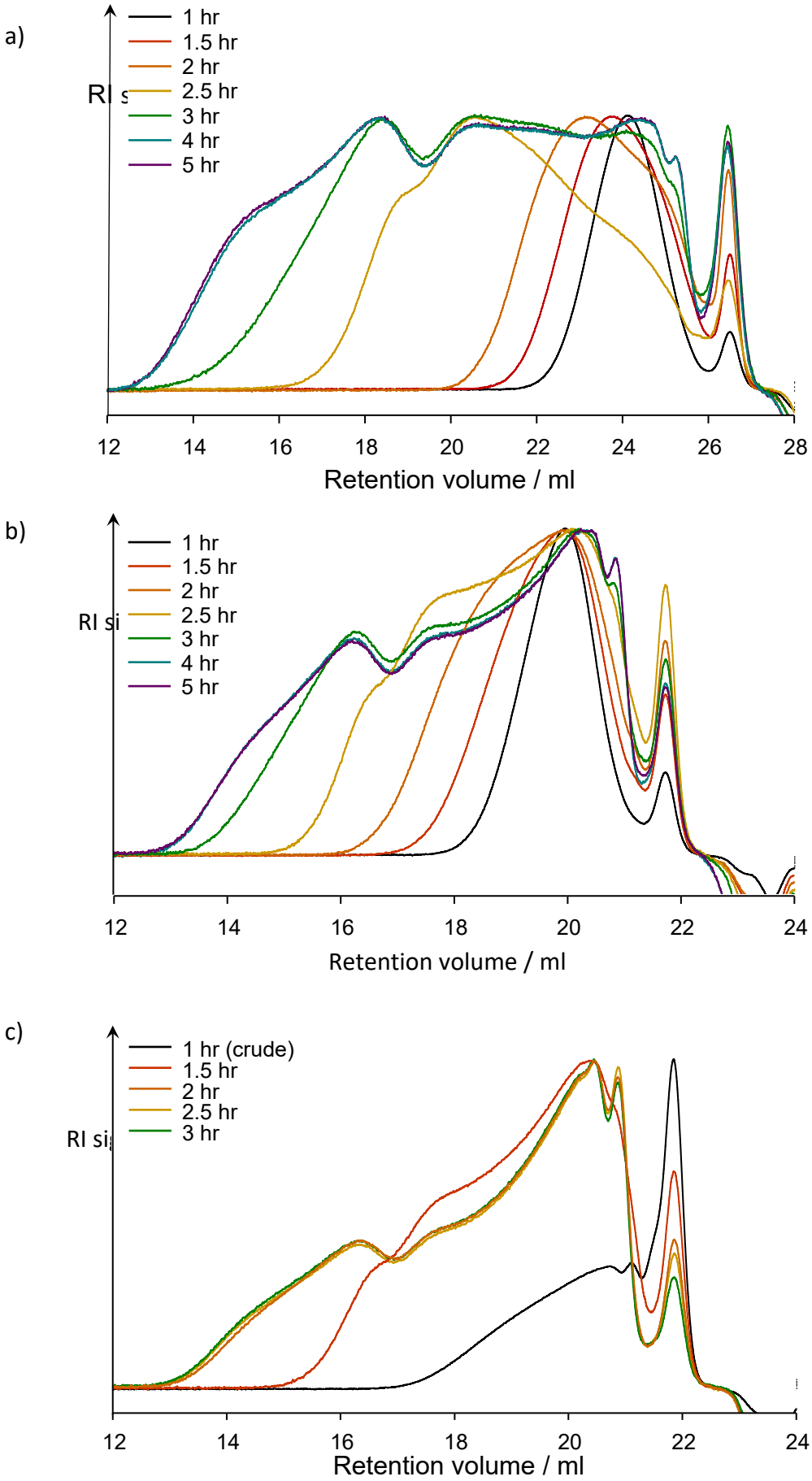


Figure S9. Overlaid RI traces for branched polymers of a) *p*($DDT_{1.00}$-$EGDMA_{0.85}$), b) *p*($DDT_{1.00}$-$HDMA_{0.70}$) and c) *p*($DDT_{1.00}$-$LDMA_{0.54}$) developing during TBRT kinetic experiments.

Table T4. ^{1}H NMR spectroscopic and TD-SEC analyses for model Mayo experiments of MMA, HMA and LMA with DDT.

			^{1}H NMR ($CDCl_3$)	TD-SEC (THF/TEA) [c]		
Monomer	Time (min)	$[DDT]_0/[Mon]_0$ [a]	Conv (%) [b]	M_n (g mol^{-1})	DP_n [d]	1 / DP_n
MMA	15	0.0115	7.4	12 818	126	0.00794
	15	0.0099	8.3	14 419	142	0.00704
	15	0.0086	9.6	16 422	162	0.00617
	15	0.0036	4.8	24 231	240	0.00417
	15	0	4.8	42 353	421	0.00238
HMA	6	0.0101	5.3	18 858	111	0.00903
	5	0.0066	4.4	24 872	146	0.00685
	5	0.0047	3.3	33 758	198	0.00504
	6	0.0033	2.9	41 485	244	0.00410
	5	0	5.8	122 717	721	0.00139
LMA	7	0.0101	8.2	23 709	92	0.01087
	7	0.0059	8.3	39 605	155	0.00645
	7	0.0041	7.0	52 582	206	0.00485
	7	0.0030	4.6	64 216	252	0.00397
	10	0	3.4	133 369	523	0.00191

[a] Calculated based on feedstock reagent masses added to reaction vessels. [b] Determined for samples taken at specified intervals referenced against sample analysed at t = 0. [c] Determined by TD-SEC using a 2% v/v TEA/THF eluent system. [d] $DP_n = (M_n - m_{DDT})/ m_{mon}$.

$$\frac{1}{DP} = \frac{1}{DP_0} + C_T \frac{[CTA]}{[M]}$$

Equation E1. Mayo Equation for calculation of chain transfer coefficient, C_T. DP = degree of polymerisation. DP_0 = degree of polymerisation in absence of CTA. [CTA] = concentration of CTA. [M] = concentration of monomer.

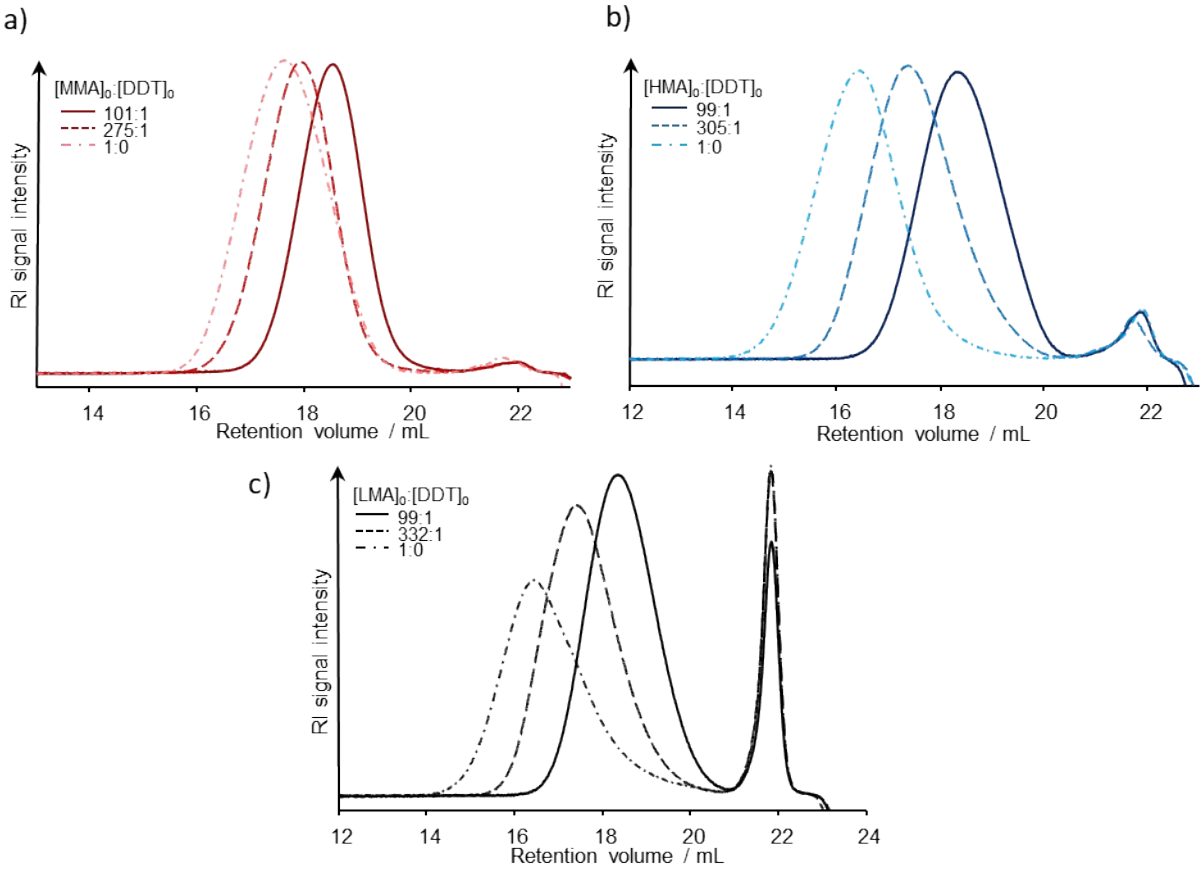


Figure S10. Overlaid RI traces for select Mayo experiments of a) MMA, b) HMA and c) LMA, displaying variation in the molecular weight distribution upon the addition of small quantities of DDT.

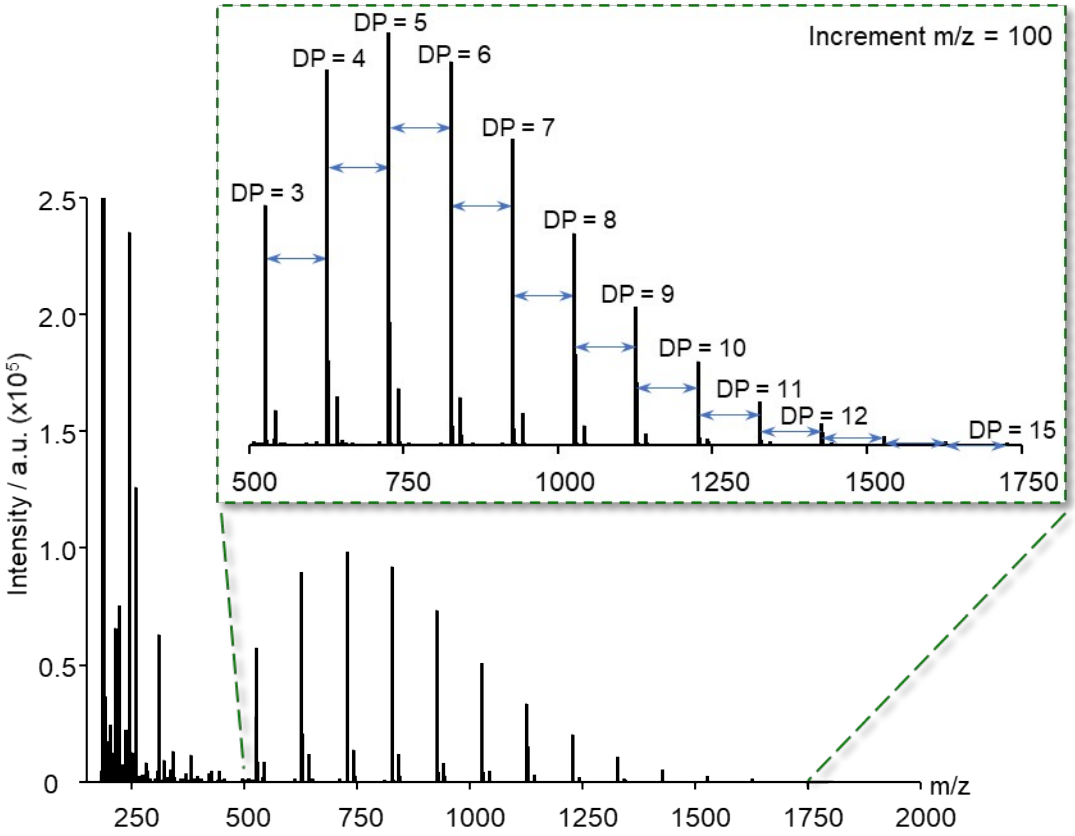


Figure S11. MALDI-TOF mass spectrum showing detectable fragments of MMA telomers.

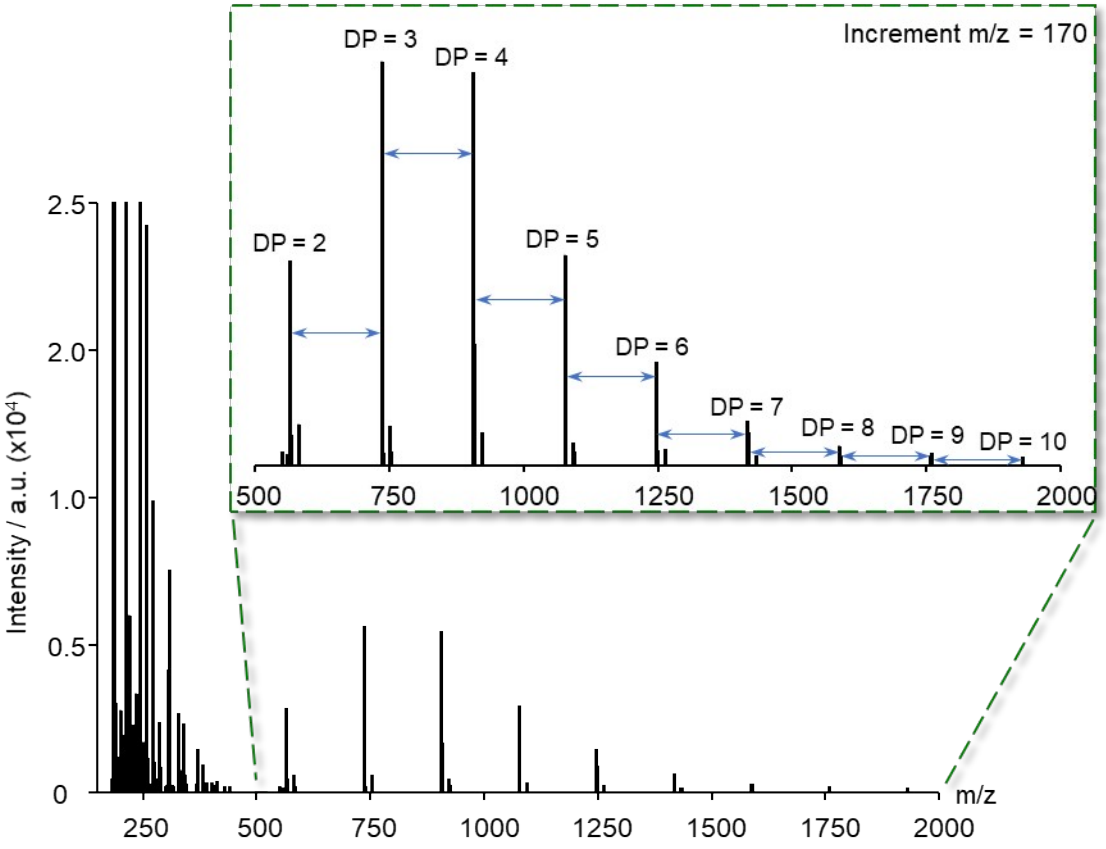


Figure S12. MALDI-TOF mass spectrum showing detectable fragments of HMA telomers.

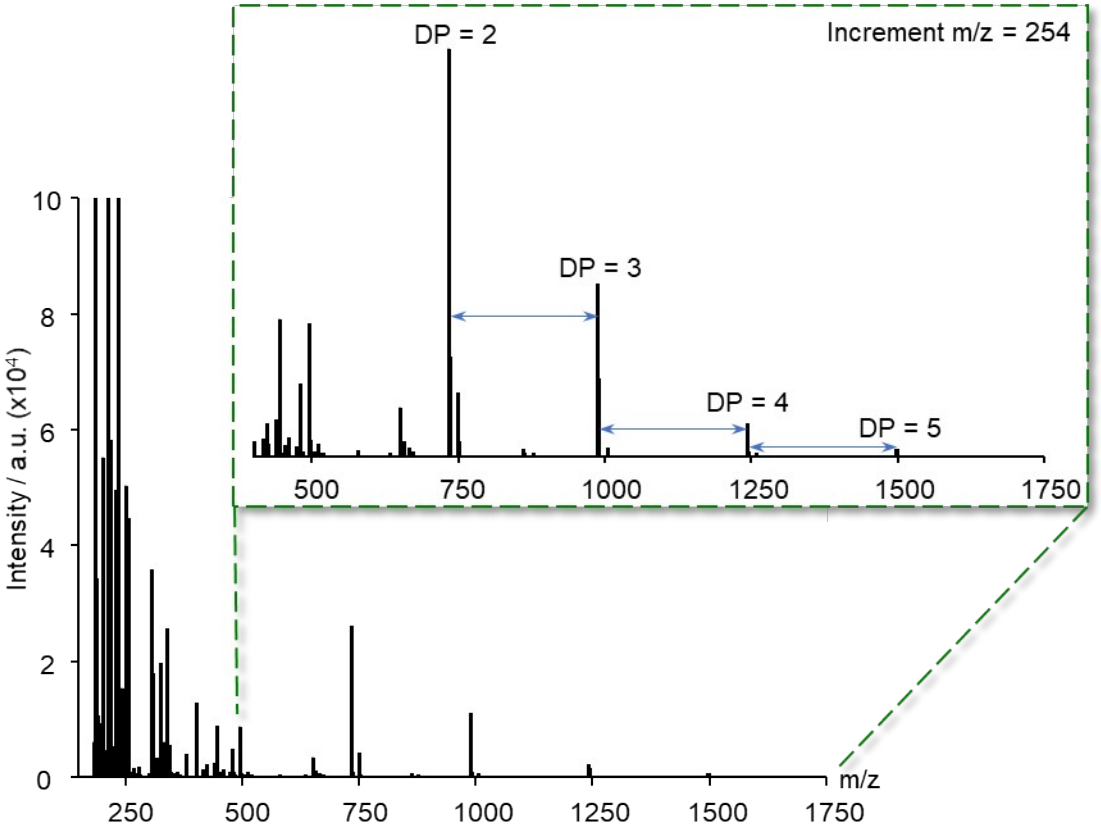


Figure S13. MALDI-TOF mass spectrum showing detectable fragments of LMA telomers.

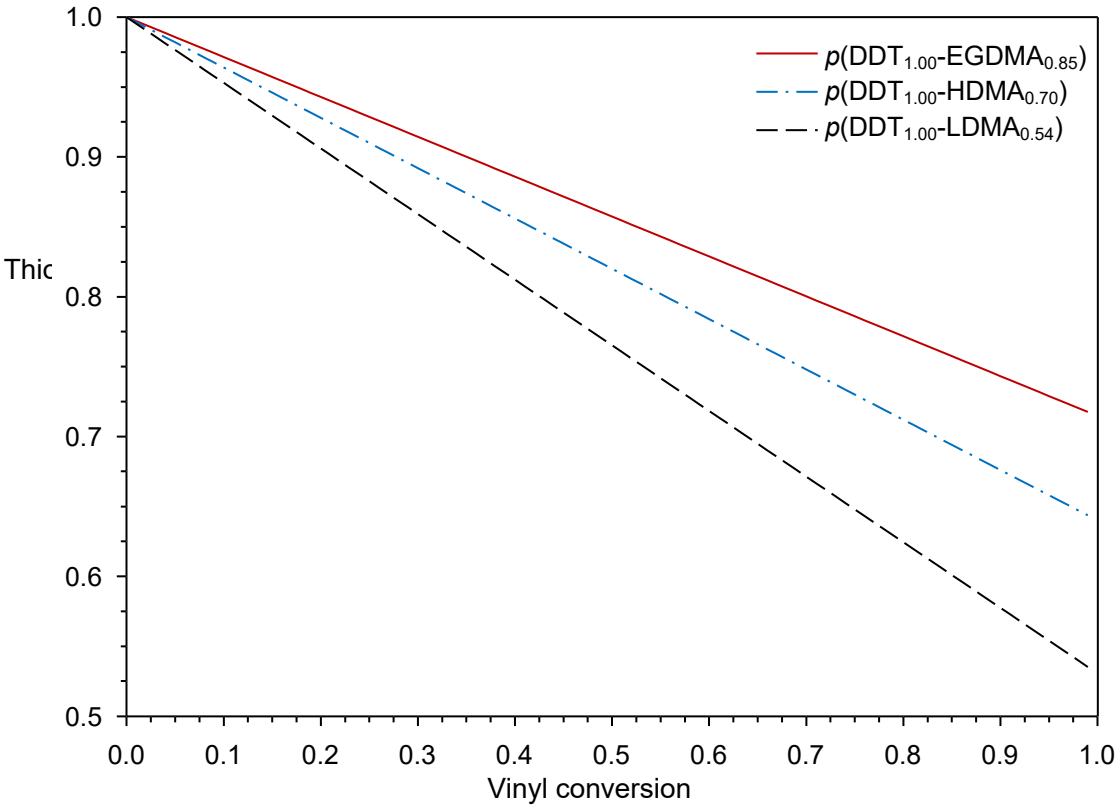


Figure S14. Theoretical calculation of thiol consumption with vinyl conversion during TBRT, based on DP_n values of 5.86, 3.89 and 2.30 obtained for linear telomers of MMA, HMA and LMA respectively, as determined by MALDI-TOF analysis.

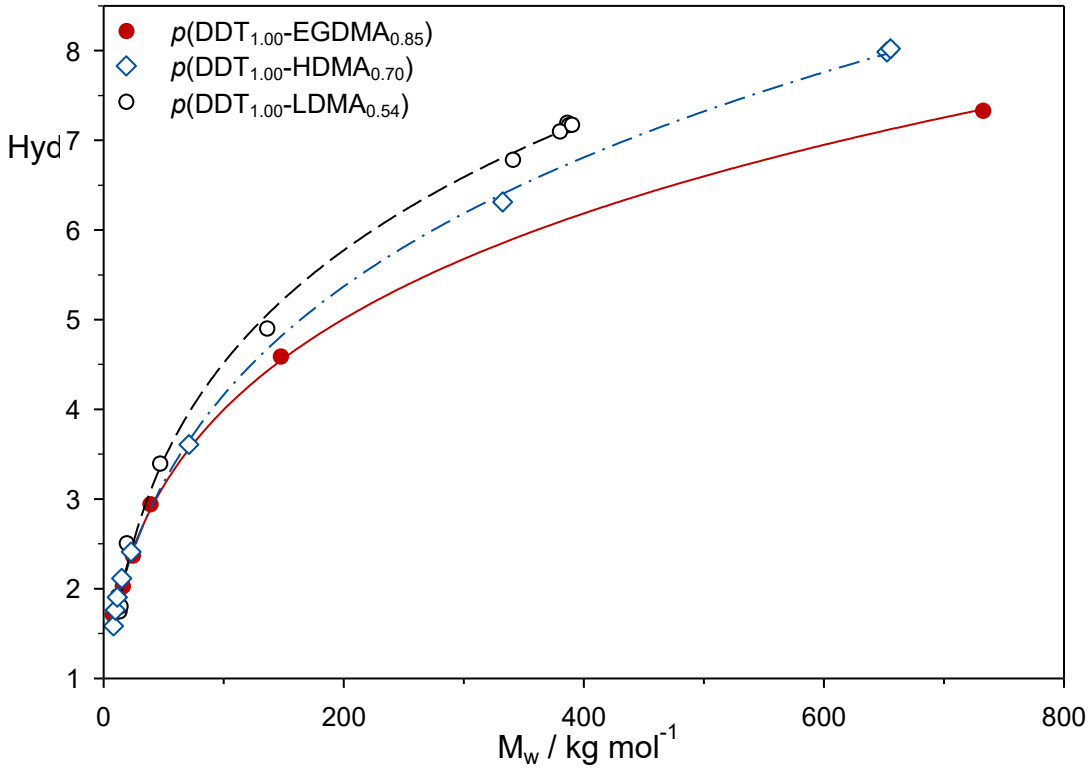


Figure S15. Monitoring the development of the hydrodynamic radius (R_H) during TBRT kinetic experiments for polymers *p*($DDT_{1.00}$-$EGDMA_{0.85}$), *p*($DDT_{1.00}$-$HDMA_{0.70}$) and *p*($DDT_{1.00}$-$LDMA_{0.54}$).

Table T5. ^{1}H NMR spectroscopic and TD-SEC analyses of fractionated samples of *p*($DDT_{1.00}$-$EGDMA_{0.85}$), *p*($DDT_{1.00}$-$HDMA_{0.70}$) and *p*($DDT_{1.00}$-$LDMA_{0.54}$).

		^{1}H NMR ($CDCl_3$)	TD-SEC (THF/TEA) [a]				
Species	Sample	[MVT]/[DDT]	M_w (g mol^{-1})	M_n (g mol^{-1})	Đ	α	dn/dc
p($DDT_{1.00}$-$EGDMA_{0.85}$)	2nd fraction	1.20	2 432 000	621 226	3.91	0.377	0.1037
	1st fraction	1.18	1 832 000	58 439	31.35	0.355	0.0898
	Initial dist	1.03	1 019 000	6 531	156.01	0.497	0.0998
p($DDT_{1.00}$-$HDMA_{0.70}$)	2nd fraction	1.17	1 552 000	102 485	15.15	0.379	0.0939
	1st fraction	1.12	1 126 000	28 559	39.44	0.362	0.0850
	Initial dist	0.99	721 009	5 771	124.94	0.366	0.0877
p($DDT_{1.00}$-$LDMA_{0.54}$)	2nd fraction	1.04	689 449	36 582	18.85	0.376	0.0835
	1st fraction	0.97	408 185	4 024	101.43	0.362	0.0818
	Initial dist	0.82	275 064	3 225	84.49	0.373	0.0819

[a] Determined by TD-SEC using a 2% v/v TEA/THF eluent system.

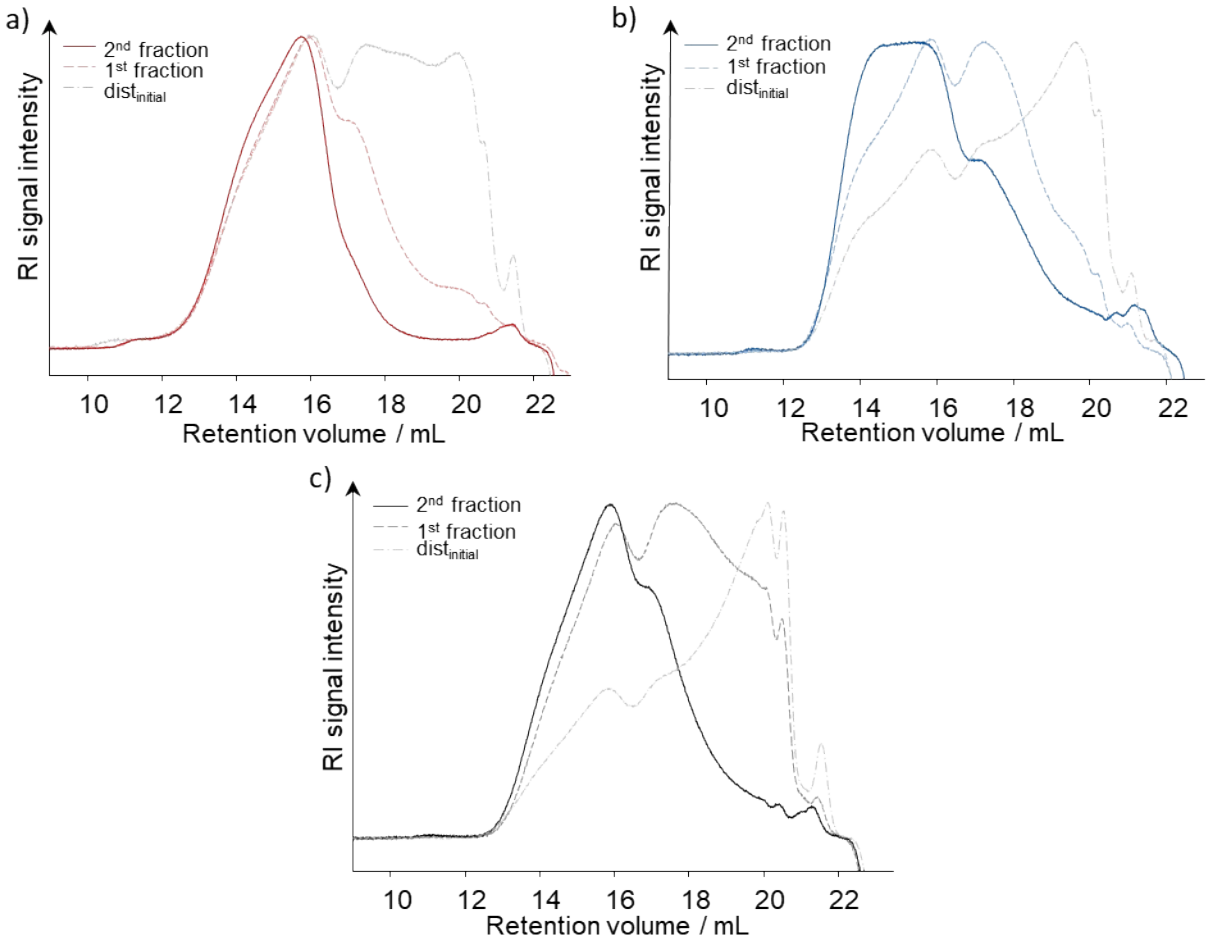


Figure S16. Overlaid RI traces for successive fractionated and original molecular weight distributions of a) $p(DDT_{1.00}\text{-}EGDMA_{0.85})$, b) $p(DDT_{1.00}\text{-}HDMA_{0.70})$ and c) $p(DDT_{1.00}\text{-}LDMA_{0.54})$.

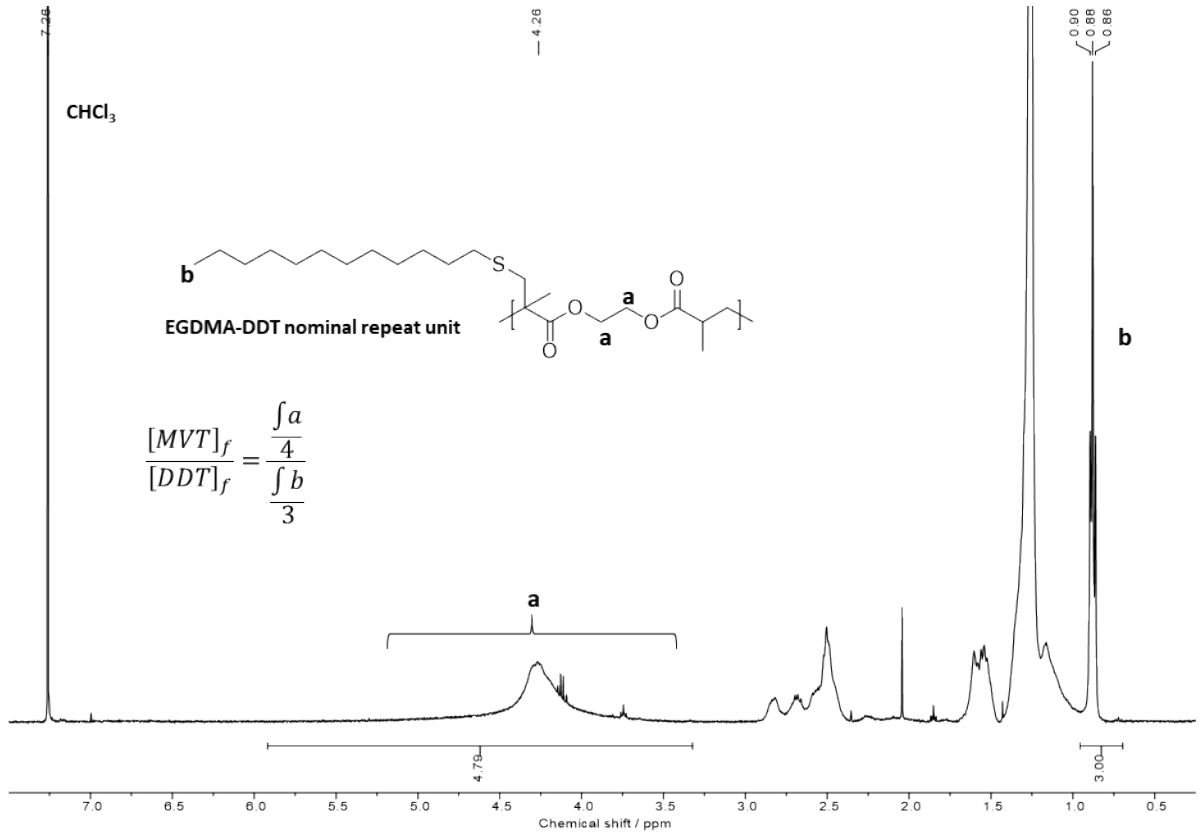


Figure S17. ^{1}H NMR spectroscopic analysis of the high molecular weight fraction of *p*($DDT_{1.00}$-$EGDMA_{0.85}$) after two fractionations. Used for calculation of [MVT]/[DDT].

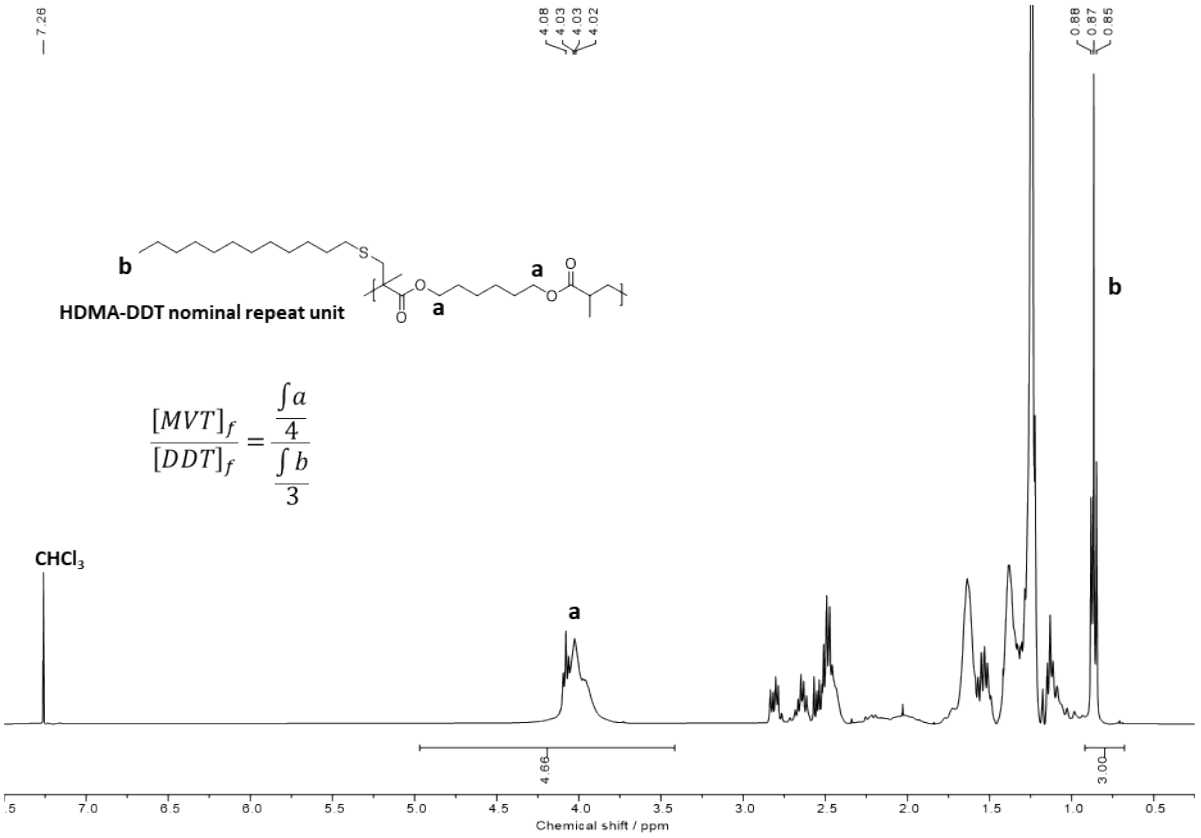


Figure S18. ^{1}H NMR spectroscopic analysis of the high molecular weight fraction of *p*($DDT_{1.00}$-$HDMA_{0.70}$) after two fractionations. Used for calculation of [MVT]/[DDT].

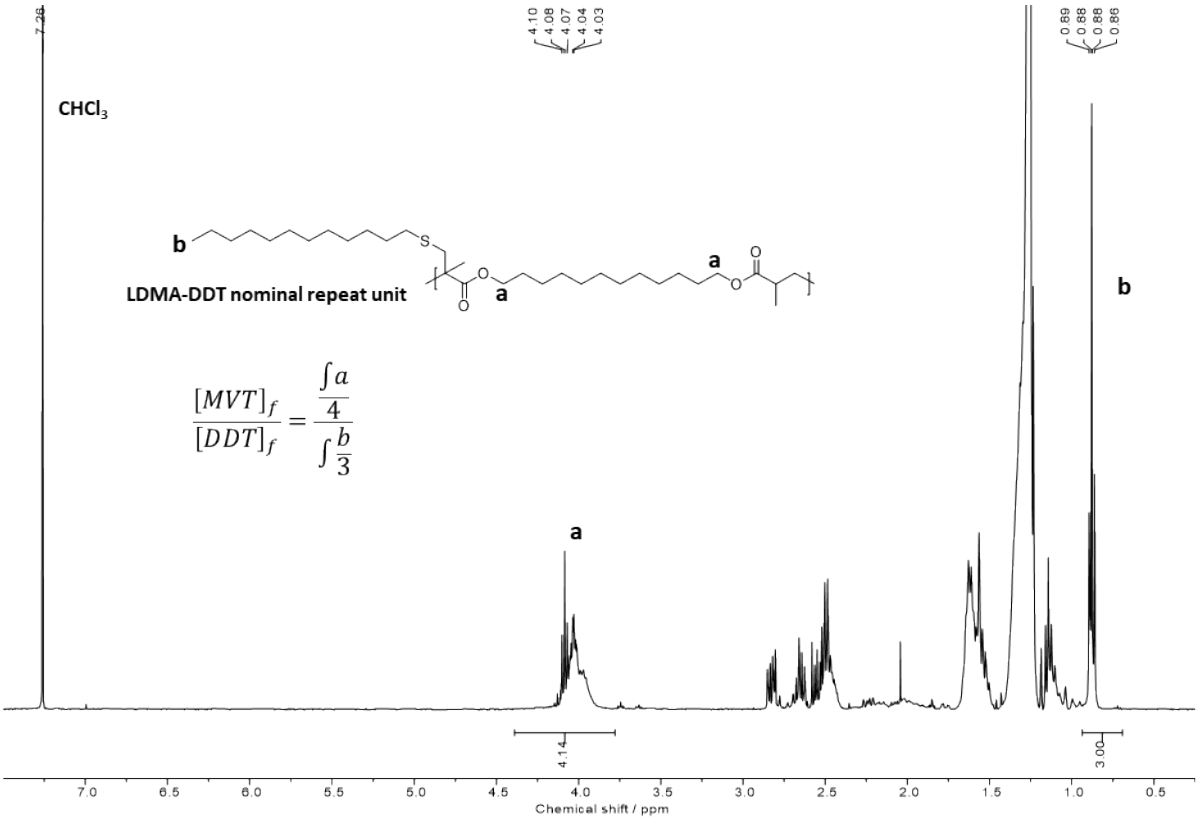


Figure S19. ^{1}H NMR spectroscopic analysis of the high molecular weight fraction of *p*($DDT_{1.00}$-$LDMA_{0.54}$) after two fractionations. Used for calculation of [MVT]/[DDT].

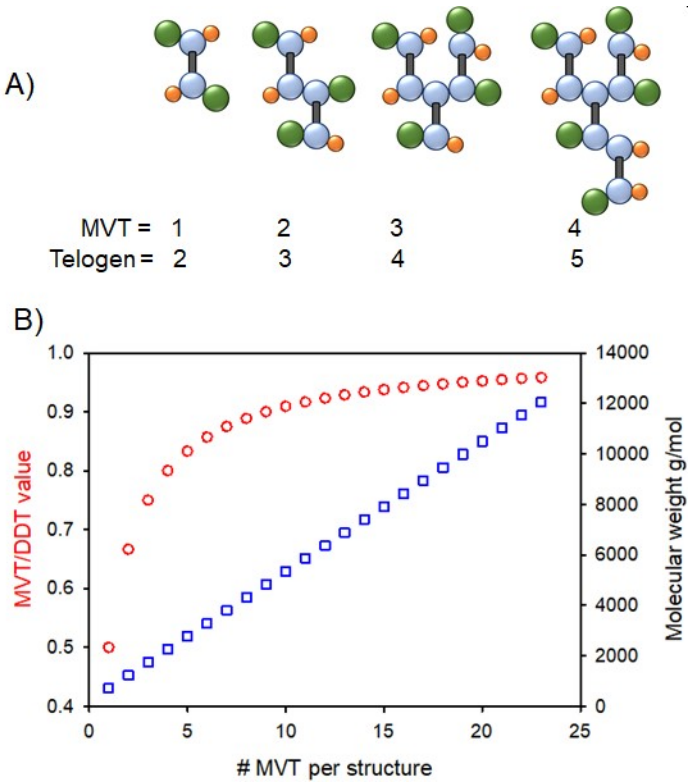


Figure S20. Illustration of MVT and telogen content within ideal TBRT polymer structures. A) demonstration of MVT and telogens in low molecular weight ideal structures; B) Variation of MVT/telogen ratio with increasing MVT per macromolecule in TBRT polymers (open red circles). Molecular weights here refer to *p*(DDT-LDMA) repeat units (open blue squares).

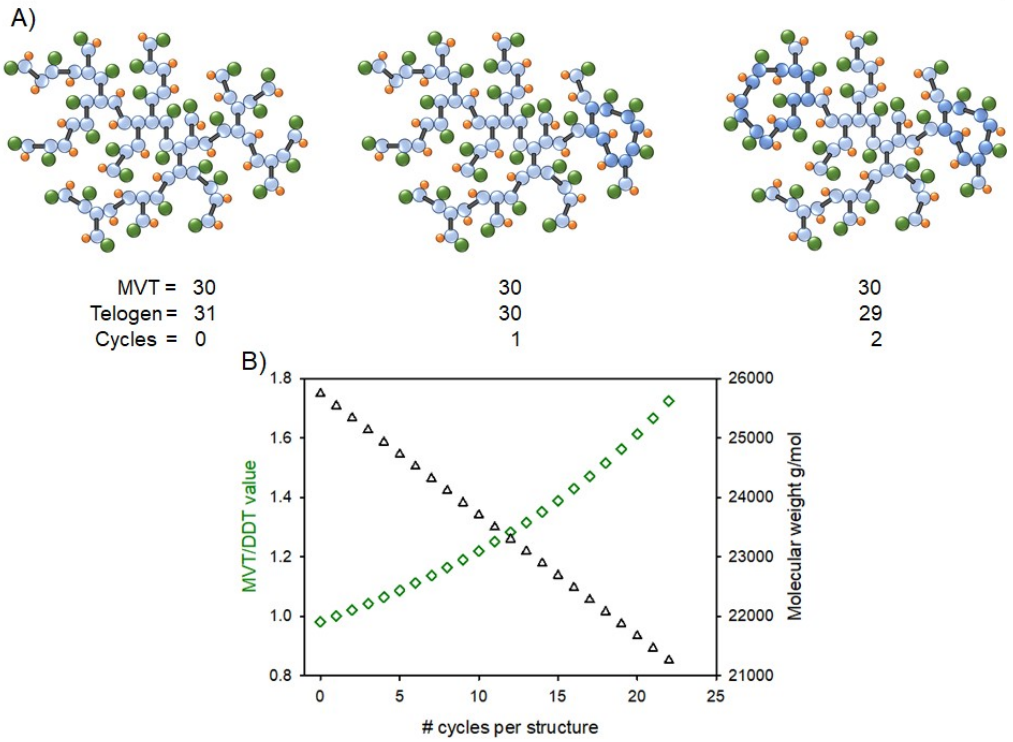
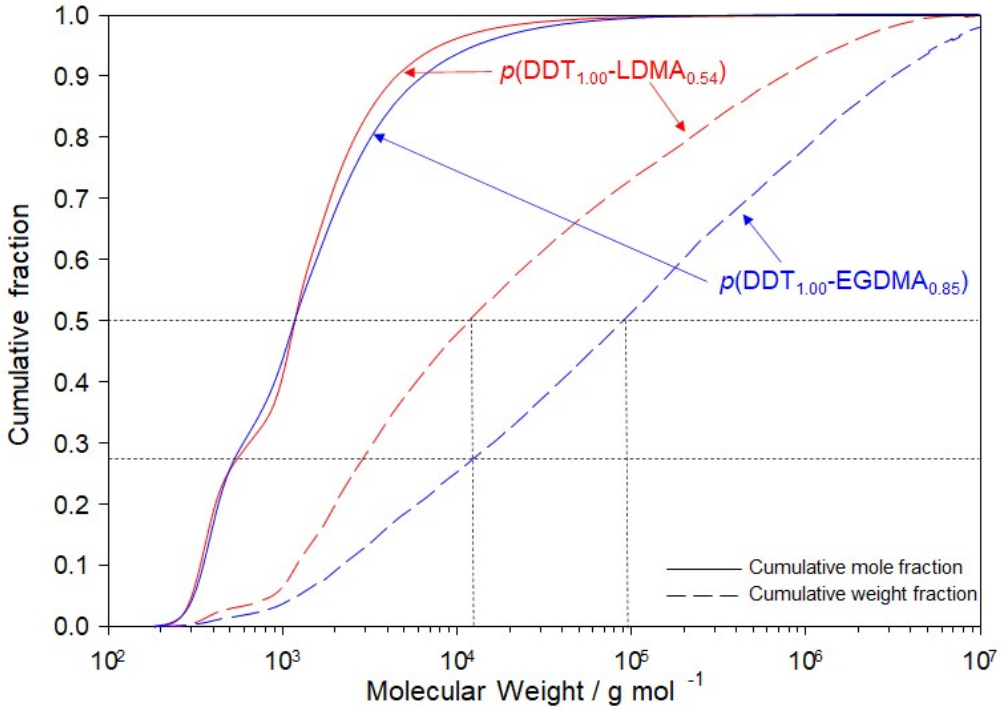


Figure S21. Illustration of variation of telogen content within ideal TBRT polymer structures in relation to cycle formation. A) schematic demonstration of MVT, telogen and cycle formation ideal structures; B) Variation of MVT/telogen ratio with increasing cycles per macromolecule in TBRT polymers (open green diamonds). Molecular weights here refer to a theoretical *p*(DDT-LDMA) polymer containing 50 MVT structures and shows



the impact of losing one DDT per cycle (open black triangles).

Figure S22. Cumulative weight and mole fraction analyses of the molecular weight distributions of *p*($DDT_{1.00}$-$LDMA_{0.54}$) and *p*($DDT_{1.00}$-$EGDMA_{0.85}$). Horizontal dotted black lines denote 50 wt% of sample (top) and the crossover weight fraction for structures of approximately 10,000 g mol^{-1} (bottom). The analysis

shows *p*($DDT_{1.00}$-$LDMA_{0.54}$) sample has considerably lower molecular weight species (relative to *p*($DDT_{1.00}$-$EGDMA_{0.85}$) with approximately 50% of the mass comprised of structures <10,000 g mol^{-1}.