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Hyperbranched polymers with step-growth chemistries from transferdominated branching radical telomerisation (TBRT) of divinyl monomers.

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1. Materials and Methods

1.1 Materials

1, 4-butanediol divinyl ether (99 %), 2, 2'-Azobis(2-methylpropionitrile) (AIBN, 98 %), 4-Nitroaniline [matrix for MALDI-TOF/MS] (4-NA, > 99 %), 4-tert-butylcatechol (\geq 99 %), α cyano-4-hyrdroxycinnamic acid [matrix for MALDI-TOF/MS] (HCCA, > 99 %), CDCl₃ (99.8 atom% D), Ethylene glycol dimethacrylate (EGDMA, 98 %), Methyl methacrylate (MMA, 99 %), Methacrylic acid (MAA, 99 %) and Trifluoroacetic acid (TFA, 99 %) 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 Methods

1.2.1 Nuclear magnetic resonance (NMR) spectroscopy

¹H and ¹³C experiments were recorded on a Bruker AMX-400 MHz spectrometer. Samples were analysed in deuterated chloroform (CDCl₃) at room temperature. Chemical shifts (δ) are reported in parts per million (ppm) relative to the known solvent residual peak (δ = 7.26 ppm). ¹³C, ¹H-HSQC (Heteronuclear Signal-Quantum Coherence), Attached Proton Test (APT) and Distortion Enhanced Polarisation Transfer using 135° decoupler pulse (DEPT-135) were also performed at 50 mg/mL. Diffusion Ordered Spectroscopy (DOSY) was performed on kinetic samples in CDCl₃. The standard Bruker double stimulated echo pulse program, with 3 spoil gradients for convection compensation was implemented. Gradient pulse (small delta, δ) was set for each sample separately between 900-1300 µs, diffusion time (big delta, Δ) was set for each sample separately between 0.20-0.25 s. DOSY experiments were run in pseudo 2D mode with a linear sequence of 16 steps with gradients strengths from 5 to 95 %. Collected spectra were processed by TopSpin 3.1 software supplied by Bruker. Diffusion coefficients for resolved ¹H signals were extracted from decay curves using the T1/T2 analyse module of the TopSpin program.

1.2.2 Triple Detection Size Exclusion Chromatography (TD-SEC)

All TD-SEC analysis of branched polymers were performed using a Malvern Viscotek instrument using GPCmax VE2001 autosampler, two Viscotek T6000M columns (and a guard column), a refractive index (RI) detector VE3580 and a 270 Dual Detector (light scattering and viscometer) with a mobile phase of THF containing 2 v/v % of triethylamine at 35 °C and a

flow-rate of 1 mL/min. All samples were dissolved at 10 mg/mL in the eluent and passed through a 200 nm syringe filter prior to injection (100 μ L). From TD-SEC results, M_n , M_w , D, molecular weight distribution and intrinsic viscosity of the polymers were estimated using the Omnisec 5.12 software. Narrow and broad polystyrene standards (Viscotek, Mw = 105 kg/mol, D = 1.022 and Mw = 245 kg/mol, D = 2.272 respectively) were used to calibrate the instrument.

All SEC analysis of telomers and oligomers were performed using a Malvern Viscotek TDA302 instrument using GPCmax VE2001 autosampler, two Viscotek T2500 columns (and a guard column) and a refractive index (RI) detector (the Dual Detector light scattering and viscometer-fitted on the instrument was not used for the calculation) with a mobile phase of THF at 35 °C and a flow-rate of 0.7 mL/min. All samples were dissolved at 10 mg/mL in the eluent and passed through a 200 nm syringe filter prior to injection (100 µL). Pure DDT was injected as the lowest molecular weight reference with a known value (202 g/mol). The molecular weights of the telomers and oligomers were determined by incrementing the molecular weight of DDT by multiples of 100 g/mol (i.e. molecular weight of MMA). Polynomial curve fits (OriginPro 2015 software) were implemented and the best fit $(r^2 = 0.9999)$ was found for a cubic function. No species were detected before a retention time of approximatively 15 minutes; the extrapolation of the cubic curve fit function to a 15 minute retention time point clearly shows that the materials formed exhibited MW < 2500 g/mol (Supplementary Figure 35), confirming MALDI and DOSY observations. The RI traces were deconvoluted using Gram-Charlier peak functions (OriginPro 2015 software) and the mass fraction of each identified species derived from the area of the deconvoluted peaks.

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 500 shots acquired in positive-reflectron mode. Cesium triiodide (CsI_3) and α-cyano-4hyrdroxycinnamic acid (HCCA) were used as the mass scale calibrant and matrix, respectively. Samples were prepared at 10 mg/mL in THF. The matrix was dissolved in THF (10 mg/mL). The solutions were combined at a 5:1 volume ratio of matrix to sample. 2 μ L of the obtained solution were deposited onto the stainless-steel sample plate and air dried. Spectra for the degradation of p(BDME) were the sum of 500 shots acquired in negative-reflectron mode. Cesium triiodide (CsI₃) and 4-Nitroaniline (4-NA) were used as the mass scale calibrant and matrix, respectively. Samples were prepared at 10 mg/mL in THF. The matrix was dissolved in THF (10 mg/mL). The solutions were combined at a 5:1 volume ratio of matrix to sample. $2 \mu L$ of the obtained solution were deposited onto the stainless-steel sample plate and air dried.

1.2.4 Elemental microanalysis

CHNS elemental analysis was recorded using a Vario Micro cube

1.2.5 Fourier-transform infrared (FT-IR)

All polymer samples were characterised using a Vertex 70 FT-IR spectrometer fitted with A225/Q platinum ATR and diamond crystal. Transmittance spectra were obtained at 16 scans/spectrum in the region from 4000 cm⁻¹ to 400 cm⁻¹ at a resolution of 4 cm⁻¹ using a deuterated triglycine sulfate and/or mercury cadmium telluride detector.

2. Experimental

2.1 TBRT of EGDMA with varying equivalents of DDT in toluene.

In a typical synthesis, EGDMA (1 g, 5.04 mmol, 1 equiv.), DDT (1.36 g, 6.73 mmol, 1.33 equiv.), AIBN (0.0248 g, 0.151 mmol) were placed into a 10 mL round-bottomed flask. Toluene was added (50 wt% based on EGDMA and DDT; 2.36 g, 2.73 mL) and the solution stirred and deoxygenated using a nitrogen purge for 15 minutes. The solution was stirred and left to telomerise at 70 °C for 24 hours. The reaction was terminated by exposure to air and cooled. The solution was precipitated into methanol (1:10 ratio) at room temperature affording a white precipitate. After drying the precipitated sample overnight under high vacuum. A sample of the product was taken for ¹H NMR spectroscopic analysis in CDCl₃ and for TD-SEC analysis in THF.

			¹ H N	MR (CDCl ₃)		TD-SEC (THF/TH	EA) ^d	
Entry	[EGDMA] ₀ / [DDT] ₀ ^a	Solvent	Conv. (%) ^b	[EGDMA] _{Final} / [DDT] _{Final} ^c	Mw (g mol ⁻¹)	Mn (g mol ⁻¹)	Ð	α	dn/dc
1	0.5	Toluene	>99.9	0.93	29 485	11 747	2.51	0.283	0.080
2	0.75	Toluene	>99.9	1.04	206 784	6 540	31.6	0.305	0.095
3	0.8	Toluene	>99.9	1.02	209 265	5 924	35.3	0.308	0.096
4	0.85	Toluene	>99.9	1.02	1 822 000	23 635	77.1	0.340	0.093
5	1	Toluene	Gel	Gel	Gel	Gel	Gel	Gel	Gel

Supplementary Table 1. Detailed analysis of the TBRT of EGDMA with DDT at 70 °C in Toluene at 50 wt.% (Initiator: 1.5 mole% AIBN based on vinyl bonds). ^a Determined by ¹H NMR of t_0 sample in CDCl₃ ^b Determined by ¹H NMR of crude sample after 24 hrs in CDCl₃ ^c Determined by ¹H NMR of purified and dried material in CDCl₃ ^d Determined by triple-detection size exclusion chromatography in THF/TEA.



Supplementary Figure 1. ¹H NMR (400 MHz, CDCl₃) of Entry 4, Supplementary Table 1 at t = 0 minutes, showing the [EGDMA]₀/[DDT]₀ = 0.85.

$$\frac{[EGDMA]_0}{[DDT]_0} = \left(\frac{\left(\frac{I_{CH_2CH_2}}{4}\right)}{\left(\frac{I_{CH_3}}{3}\right)}\right)$$

Supplementary Equation 1. Calculation of the ratio of EGMDA to DDT within the reaction mixture at t_0 . Calculations are based on comparison of the integrals from chemical shifts of EGDMA (-CH₂CH₂-, 4.0 ppm) and DDT (-CH₃, 0.88 ppm), following normalisation of the methyl group on DDT at 0.88 ppm to 3H.



7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 Supplementary Figure 2. ¹H NMR (400 MHz, CDCl₃) of Entry 4, Supplementary Table 1 at t = 24 hours (crude reaction mixture).



Supplementary Figure 3. Zoomed in region between 3.75 ppm to 7.55 ppm of Supplementary Figure 2, displaying the disappearance of vinyl resonances.

$$Vinyl Conversion (\%) = \frac{Intergral at t = 0 - Intergral at timepoint, t}{Integral at t = 0} \times 100$$

Supplementary Equation 2. Calculation of the monomer conversion of EGDMA at time point, t, by ¹H NMR analysis (400 MHz, CDCl₃). Calculations were made using the integrals from the chemical shifts at 5.5 ppm and 6.0 ppm at t = 0 and at t = t, following normalisation of the methyl group on DDT at 0.88 ppm to 3H.



Supplementary Figure 4. ¹H NMR (400 MHz, CDCl₃) of the purified sample, Entry 4, Supplementary Table 1, showing the [EGDMA]_{final}/[DDT]_{final} = 1.02.



Equation S3. Calculation of the ratio of EGMDA to DDT within the purified product. Calculations are based on comparison of the integrals from chemical shifts of EGDMA (-CH₂CH₂-, 4.0 ppm) and DDT (-CH₃, 0.88 ppm), following normalisation of the methyl group on DDT at 0.88 ppm to 3H.



Supplementary Figure 5. ¹³C NMR (green) overlaid with an APT spectra (red) (400 MHz, CDCl₃) of the purified sample, Entry 4, Supplementary Table 1.



Supplementary Figure 6. Overlay of RI traces obtained by TD-SEC analysis of Entries 1-4, Supplementary Table 1.



Supplementary Figure 7. FT-IR spectra of Entries 1-4, Supplementary Table 1: red line (Entry 1), black line (Entry 2), blue line (Entry 3), green line (Entry 4). Regions of 2200 cm⁻¹ and 1650-1550 cm⁻¹ show no detection of nitrile or vinyl groups, respectively.

Entry	С	Н	Ν	S
1	65.0	9.50	0.00	6.50
2	65.0	9.50	0.00	7.00
3	65.0	9.50	0.00	7.00
4	66.0	9.50	0.00	7.00
5	n/a	n/a	n/a	n/a

Supplementary Table 2. Elemental microanalysis of polymer samples seen in Supplementary Table 1. No N atoms were detected in the samples submitted for elemental microanalysis which indicates that no AIBN is incorporated into the final polymer structure. All results are approximate.

2.2 TBRT of EGDMA with varying equivalents of DDT in ethyl acetate.

In a typical synthesis, EGDMA (1 g, 5.05 mmol, 1 equiv.), DDT (1.36 g, 6.73 mmol, 1.33 equiv.), AIBN (0.0246 g, 0.150 mmol) were placed into a 10 mL round-bottomed flask. Ethyl acetate was added (50 wt% based on EGDMA and DDT; 2.36 g, 2.62 mL) and the solution stirred and deoxygenated using a nitrogen purge for 15 minutes. The solution was stirred and left to telomerise at 70 °C for 24 hours. The reaction was terminated by exposure to air and cooled. The solution was precipitated into methanol (1:10 ratio) at room temperature affording a white precipitate. After drying the precipitated sample overnight under high vacuum. A

			¹ H N	MR (CDCl ₃)		TD-SEC (THF/TF	CA) ^d	
Entry	[EGDMA] ₀ / [DDT] ₀ ^a	Solvent	Conv. (%) ^b	[EGDMA] _{Final} / [DDT] _{Final} ^c	Mw (g mol ⁻¹)	Mn (g mol ⁻¹)	Ð	α	dn/dc
1	0.5	EtOAc	>99.9	0.85	12 243	4 083	3.00	0.228	0.085
2	0.75	EtOAc	>99.9	1.02	129 349	4 539	28.5	0.294	0.089
3	0.8	EtOAc	>99.9	0.98	319 798	22 333	14.3	0.278	0.088
4	0.85	EtOAc	>99.9	1.00	1 578 000	13 734	115	0.337	0.088
5	1	EtOAc	Gel	Gel	Gel	Gel	Gel	Gel	Gel

sample of the product was taken for ¹H NMR spectroscopic analysis in CDCl₃ and for TD-SEC analysis in THF.

Supplementary Table 3. Detailed analysis of the TBRT of EGDMA with DDT at 70 °C in EtOAc at 50 wt.% (Initiator: 1.5 mole% AIBN based on vinyl bonds). ^a Determined by ¹H NMR of t₀ sample in CDCl₃ ^b Determined by ¹H NMR of crude sample after 24 hrs in CDCl₃ ^c Determined by ¹H NMR of purified and dried material in CDCl₃ ^d Determined by triple-detection size exclusion chromatography in THF/TEA.



Supplementary Figure 8. ¹H NMR (400 MHz, CDCl₃) of Entry 2, Supplementary Table 3 at t = 0 minutes, showing the [EGDMA]₀/[DDT]₀ = 0.75.



Supplementary Figure 9. ¹H NMR (400 MHz, CDCl₃) of Entry 7, Supplementary Table 3 at t = 24 hours (crude reaction mixture).



Supplementary Figure 10. Zoomed in region between 3.75 ppm to 7.55 ppm of Supplementary Figure 9, displaying the disappearance of vinyl resonances.



showing the $[EGDMA]_{final}/[DDT]_{final} = 1.02$.

Supplementary Figure 12. ¹³C NMR spectra (green) with DEPT-135 comparison (red) (400 MHz, CDCl₃) of the



purified sample, Entry 7, Supplementary Table 3.



Retention Volume (mL) Supplementary Figure 13. Overlay of RI traces obtained by TD-SEC analysis of Entries 1-4, Supplementary Table 1.



Supplementary Figure 14. FT-IR spectra of Entries 1-4, Supplementary Table 3: red line (Entry 1), black line (Entry 2), blue line (Entry 3), green line (Entry 4). Regions of 2200 cm⁻¹ and 1650-1550 cm⁻¹ show no detection of nitrile or vinyl groups, respectively.

3	66.0	9.50	0.00	7.50
4	65.0	9.50	0.00	7.00
5	n/a	n/a	n/a	n/a

Supplementary Table 4. Elemental microanalysis of polymer samples seen in Supplementary Table 3. No N atoms were detected in the samples submitted for elemental microanalysis which indicates that no AIBN is incorporated into the final polymer structure. All results are approximate.

2.2.1 Kinetic analysis through ¹H NMR and TD-SEC

In a kinetic study, EGDMA (10 g, 50.4 mmol, 1 equiv.), DDT (13.6 g, 67.3 mmol, 1.33 equiv.), AIBN (0.248 g, 1.5 mmol) were placed into a 100 mL round-bottomed flask. Ethyl acetate was added (50 wt% based on EGDMA and DDT; 23.6 g, 26.2 mL) and the solution stirred and deoxygenated using a nitrogen purge for 15 minutes. The solution was stirred and left to telomerise at 70 °C for 24 hours. To determine the kinetics of the reaction, samples (~ 5 mL) were taken at regular intervals and analysed by ¹H NMR and SEC. The reaction was terminated by exposure to air and cooled. The solution was precipitated into methanol (1:10 ratio) at room temperature affording a white precipitate. After drying the precipitated sample overnight under high vacuum. A sample of the product was taken for ¹H NMR spectroscopic analysis in CDCl₃ and for TD-SEC analysis in THF.

¹ H NMR (CDCl ₃)			TD-SEC (THF/TEA) ^b					
Entry	Time (minutes)	Vinyl Conversion (%) ^a	Mw (g mol ⁻¹)	Mn (g mol ⁻¹)	Ð	α	dn/dc	
1	0	0	n/a	n/a	n/a	n/a	n/a	
2°	30	48	1 167	1 004	1.16	8.65	0.059	
3	60	82	15 208	700	21.7	0.276	0.069	
4	90	91	70 543	569	124	0.325	0.072	
5	120	>99.9	142 681	1 333	107	0.316	0.073	

Supplementary Table 5. Detailed kinetic analysis of the TBRT of EGDMA with DDT at 70 °C in EtOAc at

50 wt.% (Initiator: 1.5 mole% AIBN based on vinyl bonds). ^a Determined by ¹H NMR of crude samples using Supplementary Equation 2 in CDCl₃. ^b Determined by triple-detection size exclusion chromatography in THF/TEA. ^cLALS was disregarded for the analysis of these samples.



Supplementary Figure 15. Kinetic studies of the TBRT of EGDMA with DDT at 1.5 mole% AIBN. ¹H NMR spectra (400 MHz, CDCl₃) for Entries 1-5, Supplementary Table 5.



Supplementary Figure 16. Kinetic studies of the TBRT of EGDMA (Entry 2, Supplementary Table 3): Conversion vs. time (red open circles) with corresponding semi-logarithmic plots (closed red circles); black solid line represents linear regression of semi-logarithmic plot and red dashed line guides the eye to curve.



Retention Volume (mL)

Supplementary Figure 17. Overlay of RI traces obtained by TD-SEC analysis of Entries 2-5, Supplementary Table 5. Large narrow peak on the right hand-side corresponds to free DDT.

2.2.2 Kinetic analysis through DOSY NMR

In a kinetic study, EGDMA (5 g, 25.2 mmol, 1 equiv.), DDT (6.81 g, 33.6 mmol, 1.33 equiv.), AIBN (0.124 g, 0.756 mmol) were placed into a 50 mL round-bottomed flask. Ethyl acetate was added (50 wt% based on EGDMA and DDT; 11.8 g, 13.1 mL) and the solution stirred and deoxygenated using a nitrogen purge for 15 minutes. The solution was stirred and left to telomerise at 70 °C for 24 hours. To determine the kinetics of the reaction, samples (~ 3 mL) were taken at regular intervals and analysed by DOSY NMR. The reaction was terminated by exposure to air and cooled.

		¹ H NMR (CDCl ₃)
Entry	Time (minutes)	Vinyl Conversion (%) ^a
1	0	0
2	60	75
3	90	93
4	120	>99.9

Supplementary Table 6. Detailed kinetic analysis of the TBRT of EGDMA with DDT at 70 °C in EtOAc at 50 wt.% (Initiator: 1.5 mole% AIBN based on vinyl bonds). ^a Determined by ¹H NMR of crude samples using Supplementary Equation 2 in CDCl₃



Supplementary Figure 18. DOSY NMR (400 MHz, CDCl₃) of Entry 1, Supplementary Table 6. Reactants present are highlighted: EGDMA (dashed line), DDT (round dot line) and EtOAc (dash dot line).



Supplementary Figure 19. 3D DOSY NMR (400 MHz, CDCl₃) of Supplementary Figure 18. (i) Regions 0-7.5 ppm (ii) 3.5-6.6 ppm.



Supplementary Figure 20. Resulting decay curves from DOSY NMR (400 MHz, CDCl₃) of Entry 1, Supplementary Table 6. (i) Peak at 7.26 ppm corresponding to $CDCl_3$ (ii) Peak at 6.05 ppm corresponding to the vinyl Hs on EGDMA (ii) Peak at 4.03 ppm corresponding to the -CH₂ on EtOAc (iv) Peak at 0.88 ppm corresponding to the -CH₃ on DDT.

(i)
$$D = \frac{k_B T \left(\frac{1 \cdot 5 \alpha + 1}{1 + \alpha}\right)}{6 \pi \eta \sqrt[3]{\frac{3MW}{4 \pi \rho_{\text{eff}} N_A}}} \qquad (ii) \qquad \alpha = \frac{r_s}{r} = \sqrt[3]{\frac{MW_s}{MW}}$$

Supplementary Equation 4. Equation (i) links the diffusion coefficient for a given temperature and solvent viscosity to the solute and solvent molecular masses, MW and MW_S, through a single adjustable parameter, the effective density ρ_{eff} . Equation (ii) is the ratio of the radius of the solute to that of the solvent.¹

Reactant	Diffusion Coefficient (m ² s ⁻¹)	Predicted Molecular Weight (gmol ⁻¹)
EGDMA	1.62 x 10 ⁻⁹	160
DDT	1.74 x 10 ⁻⁹	140
EtOAc	2.81 x 10 ⁻⁹	59

Supplementary Table 7. Determination of molecular weight from the diffusion coefficients determined in Supplementary Figure 15 using the Stokes-Einstein-Gierer-Wirtz Estimation (SEGWE) method.¹



Supplementary Figure 21. DOSY NMR (400 MHz, CDCl₃) spectrum of Entry 2, Supplementary Table 6.



Supplementary Figure 22. Zoomed DOSY NMR (400 MHz, $CDCl_3$) of Supplementary Figure 21 in the vinyl region (5.0 ppm – 6.5 ppm), displaying 3 different vinyl pendant species present. Molecular weights were determined from the diffusion coefficients displayed on the figure using the SEGWE method.¹



Supplementary Figure 23. 3D DOSY NMR (400 MHz, CDCl₃) of Supplementary Figure 20. (i) Regions 0-7.5 ppm (ii) 4.2-6.1 ppm.



Supplementary Figure 24. Resulting decay curves from DOSY NMR (400 MHz, CDCl₃) of Entry 2, Supplementary Table 6. (i) Peak at 7.26 ppm corresponding to $CDCl_3$ (ii) Peak at 6.05 ppm corresponding to the vinyl Hs on EGDMA (ii) Peak at 4.03 ppm corresponding to the $-CH_2$ on EtOAc (iv) Peak at 0.88 ppm corresponding to the $-CH_3$ on DDT.





Supplementary Figure 26. Zoomed DOSY NMR (400 MHz, CDCl₃) of Supplementary Figure 25 in the vinyl region (5.4 ppm – 6.15 ppm), displaying several different vinyl pendant species present. Molecular weights were determined from the diffusion coefficients displayed on the figure using the SEGWE method.¹



Supplementary Figure 27. 3D DOSY NMR (400 MHz, CDCl₃) of Supplementary Figure 25 of the region 4.0-6.7 ppm.



Supplementary Figure 28. Resulting decay curves from DOSY NMR (400 MHz, CDCl₃) of Entry 3, Supplementary Table 6. (i) Peak at 4.40 ppm corresponding to the -CH2CH2- on EGDMA (ii) Peak at 4.03 ppm corresponding to the -CH₂ on EtOAc (iv) Peak at 0.88 ppm corresponding to the -CH₃ on DDT.

2.2.3 Decreasing the concentration of radical initiator2.2.3.1 Kinetic analysis at 0.15 mole% AIBN

In kinetic study, EGDMA (10 g, 50.4 mmol, 1 equiv.), DDT (13.6 g, 67.3 mmol, 1.33 equiv.), AIBN (0.0249 g, 0.151 mmol) were placed into a 100 mL round-bottomed flask. Ethyl acetate was added (50 wt% based on EGDMA and DDT; 23.6 g, 26.2 mL) and the solution stirred and deoxygenated using a nitrogen purge for 15 minutes. The solution was stirred and left to telomerise at 70 °C for 24 hours. To determine the kinetics of the reaction, samples (~ 3 mL) were taken at regular intervals and analysed by ¹H NMR and SEC. The reaction was terminated by exposure to air and cooled. The solution was precipitated into methanol (1:10 ratio) at room temperature affording a white precipitate. After drying the precipitated sample overnight under high vacuum. A sample of the product was taken for ¹H NMR spectroscopic analysis in CDCl₃ and for TD-SEC analysis in THF.

		¹ H NMR (CDCl ₃)		TD-SEC	C (THF/TEA	A) ^b	
Entry	Time (hrs)	Vinyl Conversion (%) ^a	Mw (g mol ⁻¹)	Mn (g mol ⁻¹)	Ð	α	dn/dc
1°	0	0	n/a	n/a	n/a	n/a	n/a
2°	0.5	8	262	237	1.11	-0.961	0.606
3	1	21	1 060	314	3.38	0.741	0.058
4 ^c	1.5	33	1 378	466	2.60	0.258	0.055
5	2	46	1 879	333	5.65	0.257	0.054
6	2.5	54	2 764	1 108	2.49	0.208	0.067
7	3	60	2 850	412	6.92	0.169	0.064
8	3.5	69	4 169	169	24.6	0.186	0.065
9	4	75	5 252	124	42.2	0.222	0.074
10	5	82	12 268	923	13.3	0.241	0.074
11	6	87	24 626	397	62.0	0.264	0.076
12	24	>99.9	153 592	1 605	95.7	0.305	0.071

Supplementary Table 8. Detailed kinetic analysis of the TBRT of EGDMA with DDT at 70 °C in EtOAc at 50 wt.% (Initiator: 0.15 mole% AIBN based on vinyl bonds). ^a Determined by ¹H NMR of crude samples using Supplementary Equation 2 in CDCl₃ ^b Determined by triple-detection size exclusion chromatography in THF/TEA. ^cLALS was disregarded for the analysis of these samples.



Supplementary Figure 29. Kinetic studies of the TBRT of EGDMA with DDT at 0.15 mole% AIBN. ¹H NMR spectra (400 MHz, CDCl₃) for Entries 1-12, Supplementary Table 8.



Supplementary Figure 30. Kinetic studies of the TBRT of EGDMA at 0.15 mole% AIBN: Conversion vs. time (blue open squares) with corresponding semi-logarithmic plots (closed blue squares); black solid line represents linear regression of semi-logarithmic plot.



Supplementary Figure 31. Overlay of RI traces obtained by TD-SEC analysis of Entries 2-12, Supplementary Table 8. Large narrow peak on the right hand-side corresponds to free DDT.

2.2.3.2 Kinetic analysis at 0.05% AIBN

In kinetic study, EGDMA (12.1 g, 60.9 mmol, 1 equiv.), DDT (16.4 g, 81.2 mmol, 1.33 equiv.), AIBN (0.010 g, 0.061 mmol) were placed into a 100 mL round-bottomed flask. Ethyl acetate was added (50 wt% based on EGDMA and DDT; 28.5 g, 31.6 mL) and the solution stirred and deoxygenated using a nitrogen purge for 15 minutes. The solution was stirred and left to telomerise at 70 °C for 24 hours. To determine the kinetics of the reaction, samples (~ 3 mL) were taken at regular intervals and analysed by ¹H NMR and SEC. The

reaction was terminated by exposure to air and cooled. The solution was precipitated into methanol (1:10 ratio) at room temperature affording a white precipitate. After drying the precipitated sample overnight under high vacuum. A sample of the product was taken for ¹H NMR spectroscopic analysis in CDCl₃ and for TD-SEC analysis in THF.

Supplementary Table 9. Detailed kinetic analysis of the TBRT of EGDMA with DDT at 70 °C in EtOAc at 50 wt.% (Initiator: 0.05 % AIBN based on vinyl bonds). ^a Determined by ¹H NMR of crude samples using Supplementary Equation 2 in CDCl₃ ^b Determined by triple-detection size exclusion chromatography in THF/TEA.



Supplementary Figure 32. Kinetic studies of the TBRT of EGDMA with DDT at 0.05 mole% AIBN. ¹H NMR spectra (400 MHz, CDCl₃) for Entries 1-5, Supplementary Table 9.



Supplementary Figure 33. Kinetic studies of the TBRT of EGDMA at 0.05 mole% AIBN: Conversion vs. time (green open down triangles) with corresponding semi-logarithmic plots (closed green down triangles); black solid line represents linear regression of semi-logarithmic plot.



Supplementary Figure 34. Overlay of RI traces obtained by TD-SEC analysis of Entries 2-5, Supplementary Table 9. Large narrow peak on the right hand-side corresponds to free DDT.

			¹ H N	MR (CDCl ₃)		TD-SEC	(THF/TI	EA) ^f	
Entry	[EGDMA] ₀ / [DDT] ₀ °	% AIBN	Conv. (%) ^d	[EGDMA] _{Final} / [DDT] _{Final} ^e	Mw (g mol ⁻¹)	Mn (g mol ⁻¹)	Đ	α	dn/dc
1ª	0.75	1.5	>99.9	1.02	140 871	3 870	36.4	0.308	0.094
2ª	0.75	0.15	>99.9	1.00	144 439	3 544	40.6	0.312	0.097
3 ^b	0.75	0.05	>99.9	1.02	138 578	2 900	47.8	0.305	0.091

Supplementary Table 10. Detailed analysis of the TBRT of EGDMA with DDT at 70 °C in EtOAc at 50 wt.% varying the radical initiator (AIBN). ^a Reaction time = 24 hours. ^b Reaction time = 48 hours. ^c Determined by ¹H NMR of t_0 sample in CDCl₃. ^d Determined by ¹H NMR of crude sample after 24 hrs in CDCl₃. ^e Determined by ¹H NMR of purified and dried material in CDCl₃. ^f Determined by triple-detection size exclusion chromatography in THF/TEA.

Entry	С	Н	Ν	S
1	65.5	9.66	0.00	6.74
2	65.3	9.82	0.00	6.50
3	65.0	9.50	0.00	6.50

Supplementary Table 11. Elemental microanalysis of polymer samples seen in Supplementary Table 10. No N atoms were detected in the samples submitted for elemental microanalysis which indicates that no AIBN is incorporated into the final polymer structure. All results are approximate.



Supplementary Figure 35. Overlay of RI traces obtained by TD-SEC analysis of Entries1-3, Supplementary Table 10.



Supplementary Figure 36. FT-IR spectra of Entries 1-3, Supplementary Table 10: red line (Entry 1), blue line (Entry 2), green line (Entry 3). Regions of 2200 cm⁻¹ and 1650-1550 cm⁻¹ show no detection of nitrile or vinyl groups, respectively.

2.3 Model Reactions

2.3.1 Model Reaction 1: Telomerisation of MMA with DDT in toluene

Using the same scale in terms of double bonds as Entry 2, Supplementary Table 3.

MMA (2 g, 20.0 mmol, 1.5 equiv.), DDT (2.70 g, 13.3 mmol, 1 equiv.), AIBN (0.0493 g, 0.3 mmol) were placed into a 25 mL round-bottomed flask. Toluene was added (50 wt% based on MMA and DDT; 4.7 g, 5.43 mL) and the solution stirred and deoxygenated using a nitrogen purge for 15 minutes. The solution was stirred and left to telomerise at 70 °C for 24 hours. The reaction was terminated by exposure to air and cooled. The solution was concentrated by rotary evaporation. A sample of the product was taken for ¹H NMR spectroscopic analysis in CDCl₃, MALDI-TOF analysis and TD-SEC analysis in THF.



Supplementary Figure 37. Deconvoluted SEC chromatogram (RI) of the crude product from the telomerisation of MMA with DDT using the Gram-Charlier peak function (GCAS).



Supplementary Figure 38. Comparison of different polynomial curves (OriginPro 2015 software) for data shown in Supplementary Figure 37, a linear curve (red line), a quadratic curve (blue line) and the best fit ($r^2 = 0.9999$) was found for a cubic function (green line).



Supplementary Figure 39. MALDI-TOF spectrum of the crude product from the telomerisation of MMA with DDT demonstrating a large distribution of species varying by 100 mass units. Spectrum was acquired in positive-reflectron mode.

		Mass	(m/z)	
DP_n	$[M+H]^+$	$[M+H]^{+a}$	[M+Na] ⁺	[M+Na] ^{+ a}
1	303	319	325	342
2	403	419	425	442
3	503	519	525	542
4	603	619	625	642
5	703	719	725	742
6	-	819	825	842
7	-	919	925	942
8	-	-	1025	1042
9	-	-	1125	1142
10	-	-	1225	1242
11	-	-	1325	1342
12	-	-	1425	1442
13	-	-	1525	1542
14	-	-	1625	-
15	-	-	1725	-
16	-	-	1825	-
17	-	-	1925	-
18	-	-	2025	-
19	-	-	2125	-
20	-	-	2225	-
21	-	-	2325	-
22	-	2419	-	-

Supplementary Table 12. All species detected in MALDI-TOF analysis. ^a Species corresponding to oxidised sulphur.

2.3.1.1 Kinetic analysis at 1.5 mole% AIBN

In a kinetic study, MMA (6.08 g, 60.7 mmol, 1.5 equiv.), DDT (8.19 g, 40.5 mmol, 1 equiv.), AIBN (0.150 g, 0.911 mmol) were placed into a 50 mL round-bottomed flask. Toluene was added (50 wt% based on MMA and DDT; 14.3 g, 16.5 mL) and the solution stirred and deoxygenated using a nitrogen purge for 15 minutes. The solution was stirred and left to telomerise at 70 °C for 24 hours. To determine the kinetics of the reaction, samples (~ 3 mL) were taken at regular intervals and analysed by ¹H and DOSY NMR. The reaction was terminated by exposure to air and cooled. The solution was concentrated by rotary evaporation. A sample of the product was taken for ¹H NMR spectroscopic analysis in CDCl₃.

		¹ H NMR (CDCl ₃) ^a
Entry	Time (minutes)	Vinyl Conversion (%)
1	0	0
2	0.5	17
3	1	44
4	1.5	60
5	2	70
6	2.5	79
7	3	88
8	3.5	91
9	4	95
10	5	>99.9

Supplementary Table 13. Detailed kinetic analysis of the telomerisation of MMA with DDT at 70 °C in toluene at 50 wt.% (Initiator: 1.5 mole% AIBN based on vinyl bonds). ^a Determined by ¹H NMR of crude samples using Supplementary Equation 2 in CDCl₃.



Supplementary Figure 40. Kinetic studies of the telomerisation of MMA with DDT at 1.5 mole% AIBN. ¹H NMR spectra (400 MHz, CDCl₃) for Entries 1-10, Supplementary Table 13.



Supplementary Figure 41. Kinetic studies of the telomerisation of MMA at 1.5 mole% AIBN: Conversion vs. time (navy open triangles) with corresponding semi-logarithmic plots (closed navy triangles); black solid line represents linear regression of semi-logarithmic plot.



Supplementary Figure 42. DOSY NMR (400 MHz, CDCl₃) of Entry 1, Supplementary Table 13. Reactants present are highlighted: MMA (dashed line), DDT (round dot line) and Toluene (dash dot line).

Reactant	Diffusion Coefficient (m ² s ⁻¹)	Predicted Molecular Weight (gmol ⁻¹)
MMA	2.37 x 10 ⁻⁹	79
DDT	1.73 x 10 ⁻⁹	141
Toluene	3.02 x 10 ⁻⁹	52

Supplementary Table 14. Determination of molecular weight from the diffusion coefficients determined from Supplementary Figure 15 using the SEGWE method.¹



Supplementary Figure 43. Corresponding decay curves from DOSY NMR (400 MHz, CDCl₃) of Entry 1, Supplementary Table 13. (i) Peak at 7.26 ppm for $CDCl_3$ (ii) Peak at 5.5 ppm for vinyl Hs on MMA (iii) Peak at 0.88 ppm for $-CH_3$ on DDT.



Supplementary Figure 45. Zoomed DOSY NMR (400 MHz, CDCl₃) of Supplementary Figure 44 in the vinyl region (4.0-6.15 ppm), in displaying only free monomer.



Supplementary Figure 46. Zoomed DOSY NMR (400 MHz, $CDCl_3$) of Supplementary Figure 44 in the methyl region (3.48-3.68 ppm), displaying several different species including DP = 1 and 2.



Supplementary Figure 47. Corresponding decay curves from DOSY NMR (400 MHz, CDCl₃) of Entry 9, Supplementary Table 13. (i) Peak at 7.26 ppm for CDCl₃ (ii) Peak at 6.0 ppm for vinyl Hs on MMA (iii) Peak at 0.88 ppm for -CH₃ on DDT.

19	-	-	2125	-	-
20	-	-	2225	-	
21	-	-	2325	-	-
22	-	2419	-		
23	-	-	-	-	-
24	-	-	-	-	-
25	-	-	-	-	2726

Supplementary Table 15. A comparison of species detected in MALDI-TOF (> 99.9 % vinyl conversion, crude reaction mixture) and ¹H DOSY NMR (95 % vinyl conversion, crude reaction mixture). ^a Species corresponding to oxidised sulphur. ^b Determined through the SEGWE equation.¹

		¹ H NMR (CDCl ₃)
Entry	Time (minutes)	Vinyl Conversion (%) ^a
1	0	0
2	0.5	15

2.3.1.2 Kinetic analysis at 0.15 mole% AIBN

In a kinetic study, MMA (6.08 g, 60.7 mmol, 1.5 equiv.), DDT (8.19 g, 40.5 mmol, 1 equiv.), AIBN (0.015 g, 0.0911 mmol) were placed into a 50 mL round-bottomed flask. Toluene was added (50 wt% based on MMA and DDT; 14.3 g, 16.5 mL) and the solution stirred and deoxygenated using a nitrogen purge for 15 minutes. The solution was stirred and left to telomerise at 70 °C for 24 hours. To determine the kinetics of the reaction, samples (~ 3 mL) were taken at regular intervals and analysed by ¹H NMR. The reaction was terminated by exposure to air and cooled. The solution was concentrated by rotary evaporation. A sample of the product was taken for ¹H NMR spectroscopic analysis in CDCl₃.

3	1	25
4	1.5	33
5	2	41
6	2.5	47
7	3	55
8	3.5	57
9	4	61
10	5	70
11	6	76
12	24	>99

Supplementary Table 16. Detailed kinetic analysis of the telomerisation of MMA with DDT at 70 °C in toluene at 50 wt.% (Initiator: 0.15 mole% AIBN based on vinyl bonds). ^a Determined by ¹H NMR of crude samples using Supplementary Equation 2 in CDCl₃.



Supplementary Figure 48. Kinetic studies of the telomerisation of MMA with DDT at 1.5 mole% AIBN. ¹H NMR spectra (400 MHz, CDCl₃) for Entries 1-12, Supplementary Table 16.



Supplementary Figure 49. Kinetic studies of the telomerisation of MMA at 0.15 mole% AIBN: Conversion vs. time (orange open triangles) with corresponding semi-logarithmic plots (closed orange triangles); black solid line represents linear regression of semi-logarithmic plot.

2.3.2 Model Reaction 2: TBRT of BDME with DDT in toluene 2.3.2.1 Synthesis of 1,4-Butanediol di(methacryoyloxy)-ethyl ether (BDME)²

1, 4-butanediol divinyl ether (5.03 g, 35.4 mmol) was added to a two-necked 250 mL roundbottomed flask equipped with condenser. A small amount of 4-tert-butylcatechol (end of spatula) was added to the flask and purged with N₂ for 15 minutes. Once dissolved, the temperature was increased to 70 °C. Methacrylic acid (15.1 g, 176 mmol) was added drop-wise to the reaction mixture over a 10-minute period through a septum. The reaction proceeded at 70 °C for 6 hours, and then cooled and exposed to air. The crude product was dissolved in chloroform (25 mL) and washed with KOH solution (0.02 M, 3 x 100 mL). The combined organic washings were collected and dried over NaSO₄ and concentrated by rotary evaporator yielding a yellow oil (3.44 g, 17 %). A sample of the product was taken for ¹H NMR spectroscopic analysis in CDCl₃. ¹H NMR (400 MHz, CDCl₃): δ ppm = 1.3-1.4 (dd, 6H), 1.56-1.62 (m, 4H), 1.9 (s, 6H), 3.4-3.7 (m, 4H), 5.5 (s, 2H), 5.8-5.9 (dd, 2H), 6.0 (s, 2H).





Supplementary Figure 50. ¹H NMR (CDCl₃, 400 MHz) of pure BDME.

2.3.2.2 TBRT of BDME with DDT in toluene

BDME (2 g, 6.36 mmol, 1 equiv.), DDT (1.72 g, 8.48 mmol, 1.33 equiv.), AIBN (0.0313 g, 0.191 mmol) were placed into a 10 mL round-bottomed flask. Toluene was added (50 wt% based on BDME and DDT; 3.72 g, 4.30 mL) and the solution stirred and deoxygenated using a nitrogen purge for 15 minutes. The solution was stirred and left to telomerise at 70 °C for 24 hours. The reaction was terminated by exposure to air and cooled. A sample of the crude product was taken for ¹H NMR spectroscopic analysis in CDCl₃ and TD-SEC analysis in THF.

2.3.2.3 Degradation of *p*(BDME)

Trifluoroacetic acid (10 µL, 2 equiv.) was added to a solution of THF (9 mL) and the crude product of the 2.3.2.2 procedure (1 mL) and stirred for 72 hours at room temperature. Basic alumina (~2 g) was added to the reaction followed by filtration with a 200 nm syringe filter. A sample of the product was taken for GPC analysis in THF and Mass Spectroscopy. m/z Calcd: [M-H]⁻ (C₃₂H₅₁NaO₁₀S) = 631.6. Found: MALDI-TOF MS: [M-H]⁻ = 631.3



Supplementary Figure 51. Schematic representation of the formation of an acid-sensitive polymer from the TBRT of BDME and DDT and the degradation of the BDME-derived polymer to its telomer chains by acid cleavage (red lines) using trifluoroacetic acid (TFA).



Supplementary Figure 52. RI traces before and after cleavage (24 hrs and 72 hrs) of crude p(BDME).



Mass (m/z) Supplementary Figure 53. MALDI-TOF analysis of crude p(BDME) after degradation. Spectrum was acquired in negative-reflectron mode.

_	Mass	s (m/z)			
DP_n	[M-H] ⁻	[M-H] ⁻ a			
1	-	-			
2	373	389			
3	459	475			
4	545	561			
5	631	647			
6	717	733			
7	803	819			
8	889	-			
9	975	991			
10	1061	-			
11	1147	-			
12	1233	-			
13	1319	-			
			Table	17.	Specie

Supplementary

detected in MALDI-TOF. ^a Species corresponding to oxidised sulphur.

2.4 Theoretical Considerations



Supplementary Figure 54. Theoretical considerations of the variations in telogen/taxogen ratio (blue) and kinetic chains lengths (red) as HbP structure increases in size.

3. References

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- 2. Ruckenstein, E. & Zhang, H. A Novel Breakable Cross-Linker and pH-Responsive Star-Shaped and Gel Polymers. **32**, 3979–3983 (1999).