Employing Transfer-dominated Branching Radical Telomerisation (TBRT) and Atom Transfer Radical Polymerisation (ATRP) to form complex polyester-polymethacrylate branched-linear star copolymer hybrids *via* orthogonal initiation.

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Supplementary Information:

Contents

1. Materials & Methods of Characterisation

1.1 Materials

All chemicals were used as received. 2-hydroxyethyl methacrylate (HEMA, >99%, ≤500 ppm monomethyl ether hydroquinone (MEHQ) as inhibitor); 4-(dimethylamino)pyridine (DMAP, ≥99%); dichloromethane (DCM, anhydrous, ≥99.8%, 40-150 ppm amylene as stabiliser); chloroform-d (CDCl3, 99.8% D); 1-dodecanethiol (DDT, ≥98%); 2,2'-azobis(2-methylpropionitrile) (AIBN, 98%); copper (I) chloride (≥99.995% trace metals basis); 4,4'-dinonyl-2,2'-dipyridyl (dNbpy, 97%); toluene (anhydrous, 99.8%); methyl methacrylate (MMA, 99%, ≤30 ppm MEHQ as inhibitor); butyl methacrylate (BMA, 99%, 10 ppm MEHQ as inhibitor); hexyl methacrylate (HMA, 98%, 100 ppm MEHQ as inhibitor); cyclohexyl methacrylate (cHMA, ≥97%, 60 ppm MEHQ as inhibitor); lauryl methacrylate (LMA, 96%, 500 ppm MEHQ as inhibitor); aluminium oxide (activated, neutral, Brockmann Activity I); monomethyl ether hydroquinone (MEHQ, 99%, reagent plus) were obtained from Merck (Sigma-Aldrich). 2-bromoisobutyryl bromide (BIBB, 97%); triethylamine (TEA, 99%); magnesium sulfate ($MgSO_4$, dried, lab reagent grade) were sourced from Thermo Fisher Scientific. Ethyl acetate (EtOAc, ≥99.8%, analytical reagent grade); tetrahydrofuran (THF, 99.5%, laboratory reagent grade); methanol (≥99.9%, analytical reagent grade); petroleum ether (40-60 ℃, laboratory reagent grade); sodium hydrogen carbonate (99.7%, analytical reagent grade); hydrochloric acid (~37%) were acquired from Fisher Scientific. Ethylene glycol dimethacrylate (EGDMA, 98%, 100 ppm MEHQ as inhibitor) was sourced from Alfa Aesar. Silica gel (60, 40-63 μm) was obtained from VWR International.

1.2 Methods of Characterisation

1.2.1 NMR Spectroscopy

^{1}H, COSY, ^{13}C, APT and HSQC NMR spectra were recorded using the University of Liverpool Bruker Avance III HD DEPT400 (400 MHz) NMR spectrometer and the Materials Innovation Factory Bruker Avance III (400 MHz) NMR spectrometer. All the samples were analysed using chloroform-d at room temperature. ^{1}H NMR measurements were made at 400 MHz and ^{13}C NMR measurements were made at 100 MHz, with the chemical shifts recorded in ppm. All the spectra were processed using MestReNova 14.0 software or TopSpin 4.0.9 software.

1.2.2 TD-SEC

Size exclusion chromatography was conducted using a Malvern Viscotek TDA 302 instrument equipped with a GPCmax VE2001 auto-sampler, a triple detector array TDA 305 (refractive index, light scattering and viscometer) and two Viscotek columns (2 x C6000M plus guard column). Size exclusion chromatography was performed at 35 °C at a flow rate of 1 mL min^{-1} using $CHCl_3$ as the mobile phase.

1.2.3 DSC

All DSC data were acquired using a TA Instruments Discovery Series DSC25 equipped with an RCS90 cooling unit, TZero aluminium hermetic lids and TZero aluminium pans. Unless otherwise specified, all DSC measurements were taken using a heating rate of 20 ℃ per min, and a cooling rate of 10 ℃ per min, in the temperature range -80 ℃ to 175 ℃. All the data was recorded using TA Instruments software, TRIOS 5.1.1.46572.

1.2.4 Mass Spectrometry

Chemical ionisation mass spectrometry was measured using an Agilent 7200 Accurate Mass QTOF.

1.2.5 MALDI-TOF

The MALDI-TOF measurement of the linear telomer was made using the Materials Innovation Factory Bruker Autoflex Mass Spectrometer. The spectrum was the sum of 500 shots acquired in positive-reflection mode. Caesium triiodide and α-cyano-4-hydroxycinnamic acid were used as the mass scale calibrant and matrix, respectively. The sample and matrix were prepared at 10 mg/mL in THF. The sample and matrix were combined at a 5:1 volume ratio of matrix to sample. 2 μL of the combined solution was placed onto a stainless-steel sample plate and air dried.

2. Experimental Methods

2.1 BBEMA Synthesis

DMAP (1.41 g, 11.53 mmol, 0.1 equiv.), TEA (17.49 g, 172.89 mmol, 1.5 equiv.), HEMA (15.00 g, 115.26 mmol, 1 equiv.) and anhydrous THF (110 mL) were added to a 500 mL round bottom flask fitted with a 250 mL pressure-equalising dropping funnel and magnetic stirrer bar (2.5 mm) under an inert nitrogen atmosphere. The solution was cooled to approximately 0 ℃ for ~20-30 minutes using an ice-bath. Anhydrous THF (90 mL) was added to the closed dropping funnel followed by BIBB (39.75 g, 172.89 mmol, 1.5 equiv.). The contents of the dropping funnel were added to the reaction flask dropwise over a period of ~30 minutes, forming a white coloured mixture. The reaction was left to stir overnight under a nitrogen atmosphere at ambient temperature.

This was worked up by adding water (5-10 mL) dropwise before allowing the mixture to stir at ambient temperature. The precipitate was removed by gravity filtration and was subsequently washed with a small volume of THF. The filtrate was concentrated by rotary evaporation to remove the reaction solvent. The crude mixture was dissolved in DCM (500 mL) and washed with 0.1 M HCl aq. (3 x 100 mL), saturated $NaHCO_3$ (3 x 100 mL) and water (2 x 100 mL). The organic solution was then dried over $MgSO_4$ and filtered by gravity. This was followed by the addition of a radical inhibitor, MEHQ (~15 mg) prior to temporary storage (in the absence of light).

The crude product was rotary evaporated to remove DCM before being purified by flash column chromatography using silica gel and an eluent consisting of EtOAc and petroleum ether (gradient elution, 0/100 – 10/90). The eluted fractions containing the BBEMA product were combined, and MEHQ (~10 mg) was added before the solution was rotary evaporated to remove the eluent. Finally, the product was dried by freeze-drying to give pure BBEMA (11.98 g, 37.2%) as a clear-yellow viscous oil. The pure BBEMA was stored permanently in a fridge (in the absence of light). δH (400 MHz; $CDCl_3$; Me_4Si) 6.15 (1 H, s, CH3C(=C*H*H)C(O)O-), 5.61 (1 H, s, CH3C(=CH*H*)C(O)O-), 4.44 (4 H, m, -OC*H*2C*H*2O-), 1.96 (3 H, s, C*H*3C(=CH2)C(O)O-), 1.95 (6 H, s, -OC(O)C(C*H*3)2Br). δC (100 MHz; CDCl3; Me4Si) 171.44 (-O*C*(O)C(CH3)2Br), 167.01 (CH3C(=CH2)*C*(O)O-), 135.86 (CH3*C*(=CH2)C(O)O-), 126.16 (CH3C(=*C*H2)C(O)O-), 63.51 (-O*C*H2CH2O-), 61.90 (-OCH2*C*H2O-), 55.33 (-OC(O)*C*(CH3)2Br), 30.66 (-OC(O)C(*C*H3)2Br), 18.24 (*C*H3C(=CH2)C(O)O-). *m/z* (CI) 298 ([M+NH3]+, 85%), 296 ([M+NH3]+, 85), 281 (M+, 4), 279 (M+, 4), 216 (13), 113 (100), 69 (2).

2.2 p(DDT-EGDMA) Synthesis

EGDMA (2.00 g, 10.2 mmol, 0.850 equiv.), DDT (2.404 g, 11.9 mmol, 1.00 equiv.), AIBN (0.0496 g, 0.301 mmol) and EtOAc (50 wt.% based on EGDMA and DDT; 4.404 g) were added to a 25 mL round-bottom flask with a magnetic stirrer bar. The solution was purged with nitrogen and stirred for ~15 minutes. An aliquot (~100 μL) of the reaction solution was taken for ^{1}H NMR analysis prior to lowering the flask into the heating block to initiate the polymerisation. The reaction was stirred at 70 °C for ~24 hours

before being stopped via cooling and exposure to air. A second aliquot (~100 μL) of the reaction mixture was taken to determine vinyl conversion by ^{1}H NMR analysis. The reaction mixture was diluted in THF and precipitated into methanol at ambient temperature under constant agitation, using a good solvent to anti-solvent ratio of 1:10. The precipitation formed a white polymer precipitate. This was then re-dissolved in THF and precipitated into methanol for a second time, producing a white polymer precipitate. The polymer was dried in a vacuum oven at 40 ℃ overnight to give p(DDT-EGDMA) (1.72 g) as a white solid.

2.3 p([DDT-MMA]-*stat*-BBEMA) Synthesis

MMA (1.011 g, 10.2 mmol, 1.7 equiv.), BBEMA (1.409 g, 5.1 mmol, 0.850 equiv.), DDT (1.202 g, 5.94 mmol, 1.000 equiv.), AIBN (0.0377 g, 0.2295 mmol) and EtOAc (50 wt.% based on MMA, BBEMA and DDT; 3.622 g) were added to a 25 mL round-bottom flask with a magnetic stirrer bar. The solution was purged with nitrogen and stirred for ~15 minutes. An (~100 μL) aliquot of the reaction solution was taken prior to initiation to determine vinyl conversion. The flask was then placed on a hotplate and was kept at 70 ℃ with constant stirring for ~24 hours. The reaction was stopped via cooling and exposure to air. A second aliquot (~100 μL) of the reaction mixture were taken to determine vinyl conversion. The reaction mixture was freeze dried to give p([DDT-MMA]-*stat*-BBEMA) as a yellow viscous oil.

2.4 p([DDT-EGDMA]-*stat*-BBEMA) Macroinitiator Synthesis

EGDMA (1.00 g, 5.1 mmol, 0.850 equiv.), BBEMA (1.409 g, 5.1 mmol, 0.850 equiv.), DDT (1.202 g, 5.94 mmol, 1.000 equiv.), AIBN (0.0377 g, 0.2295 mmol) and EtOAc (50 wt.% based on EGDMA, BBEMA and DDT; 3.611 g) were added to a 25 mL round-bottom flask with a magnetic stirrer bar. The solution was purged with nitrogen and stirred for ~15 minutes. These steps were repeated two more times, producing a total of three separate reaction vessels. An aliquot from each of the reaction mixtures was taken prior to initiation to determine the molar ratios. The flasks were then placed on a hotplate and were each kept at 70 ℃ with constant stirring for ~24 hours. All three reactions were stopped via cooling and exposure to air. A second aliquot of the reaction mixtures were taken to determine vinyl conversions. Each reaction mixture was diluted in THF, then combined before precipitation into methanol (using a good solvent to anti-solvent ratio 1:15) at ambient temperature under constant agitation. The precipitation formed a white-yellow polymer precipitate. This was then re-dissolved in THF and precipitated into methanol for a second time, producing a white-yellow polymer precipitate. The polymer was dried in a vacuum oven at 40 ℃ overnight to give p([DDT-EGDMA]-*stat*-BBEMA) (6.46 g) as a clear-yellow solid.

2.5 p(([DDT-EGDMA]-*stat*-BBEMA)-monomer) Synthesis

p([DDT-EGDMA]-*stat*-BBEMA) macroinitiator (0.136 g, 0.1998 mmol, 1.00 equiv.) and 4,4'-dinonyl-2,2'-dipyridyl (dNbpy) (0.163 g, 0.3996 mmol, 2.00 equiv.) were added to a 25 mL round bottomed flask equipped with a magnetic stirrer bar. An excess of monomer and anhydrous toluene were purged with nitrogen in separate flasks for ~25 minutes. Monomer (x g, 9.99 mmol, 50.0 equiv.) and anhydrous toluene (50 wt.% wrt. monomer, p([DDT-EGDMA]-*stat*-BBEMA) macroinitiator, dNbpy and Cu(I)Cl, y g, z mL) were then added to the reaction flask whilst maintaining a positive nitrogen flow. The resultant mixture was stirred and purged with nitrogen for a further ~20 minutes. Cu(I)Cl (19.8 mg, 0.1998 mmol, 1.00 equiv.) was rapidly added to the flask whilst maintaining a positive nitrogen flow, immediately forming a dark brown solution. The reaction mixture was subsequently bubbled with nitrogen for ~5 minutes, sealed and left stirring overnight on a hotplate at 60 ℃. The polymerisation was terminated by cooling, exposure to air and the addition of THF (10 mL) to poison

the catalyst. An aliquot of the reaction mixture was taken prior to poisoning with THF but after cooling/ exposure to air in order to determine vinyl conversion by ^{1}H NMR analysis. The solution was left to stir overnight to ensure the complete poisoning of the catalytic system. The green polymer solution was passed through a neutral alumina column to remove the catalytic system using THF as the mobile phase. The solution was then concentrated and precipitated into a cold methanol (using a good solvent to anti-solvent ratio 1:15). The resultant polymer precipitate was dried in a vacuum oven at 40 ℃ overnight to give p(([DDT-EGDMA]-*stat*-BBEMA)-monomer) (v g) as a w. Note that entry 1 and 4 (see Table S1) required Buchner filtration post-precipitation as the precipitate emerged as a suspension. See Table S1 for details about the chosen monomers, anhydrous toluene, the nature of the polymer products and their yield.

Table S1: Entries for each ATRP reaction performed using the reaction procedure outlined above.

Entry	Monomer	Monomer Mass	Anhyd. Toluene		Product Description	Yield
			Mass	Volume		
		***x* (g)**	***y* (g)**	***z* (mL)**	***w***	***v* (g)**
1	MMA	1.00	1.3188	1.52	Course white powder	0.80
2	BMA	1.42	1.7388	2.01	White solid	0.97
3	HMA	1.70	2.0188	2.33	Clear-yellow solid	1.30
4	cHMA	1.68	1.9988	2.31	Fine white powder	1.56
5	LMA	2.54	2.8588	3.30	Clear-yellow solid	2.36

2.6 Kinetics Experiment

p([DDT-EGDMA]-stat-BBEMA) macroinitiator (0.112 g, 0.1652 mmol, 1.00 equiv.) and dNbpy (0.135 g, 0.3303 mmol, 2.00 equiv.) were added to a 25 mL round bottomed flask equipped with a magnetic stirrer bar. An excess of lauryl methacrylate and anhydrous toluene were purged with nitrogen in separate flasks for ~25 minutes. Lauryl methacrylate (2.10 g, 8.26 mmol, 50.0 equiv.) and anhydrous toluene (50 wt.% wrt. lauryl methacrylate, p([DDT-EGDMA]-stat-BBEMA) macroinitiator, dNbpy and Cu(I)Cl, 2.3634 g, 2.73 mL) were then added to the reaction flask whilst maintaining a positive nitrogen flow. The resultant solution was purged with nitrogen for a further ~ 20 minutes (with constant stirring). Cu(I)Cl (16.4 mg, 0.1652 mmol, 1.00 equiv.) was rapidly added to the flask whilst maintaining a positive nitrogen flow, immediately forming a dark brown solution. The reaction mixture was subsequently bubbled with nitrogen for ~ 5 minutes, sealed and placed on a hotplate at 60 ℃ with constant stirring. Aliquots (~100 μL) of the reaction mixture were taken at intervals throughout the duration of the reaction. Special care was taken to maintain the nitrogen atmosphere and avoid premature poisoning of the catalytic system. The polymerisation was terminated by cooling and exposure to air, before then taking a final aliquot of the reaction mixture.

3. Supplementary Figures and Tables

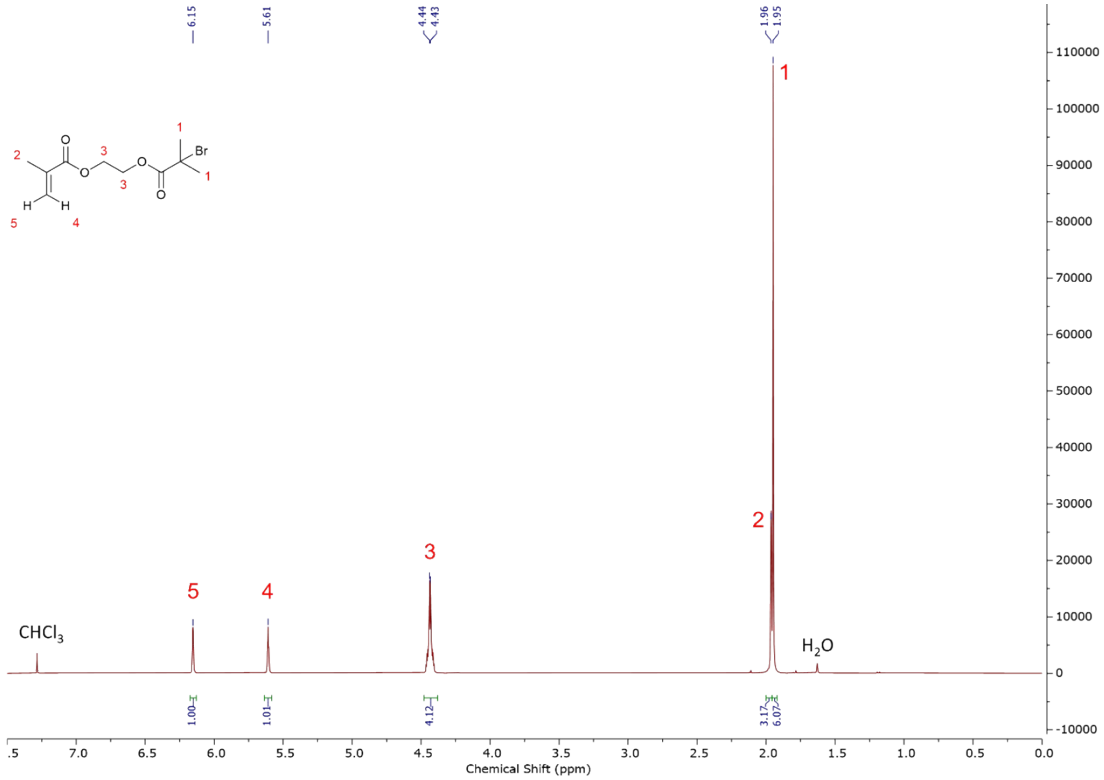


Figure S1: ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of 2-(α-bromoisobutyryloxy)ethylmethacrylate (BBEMA).

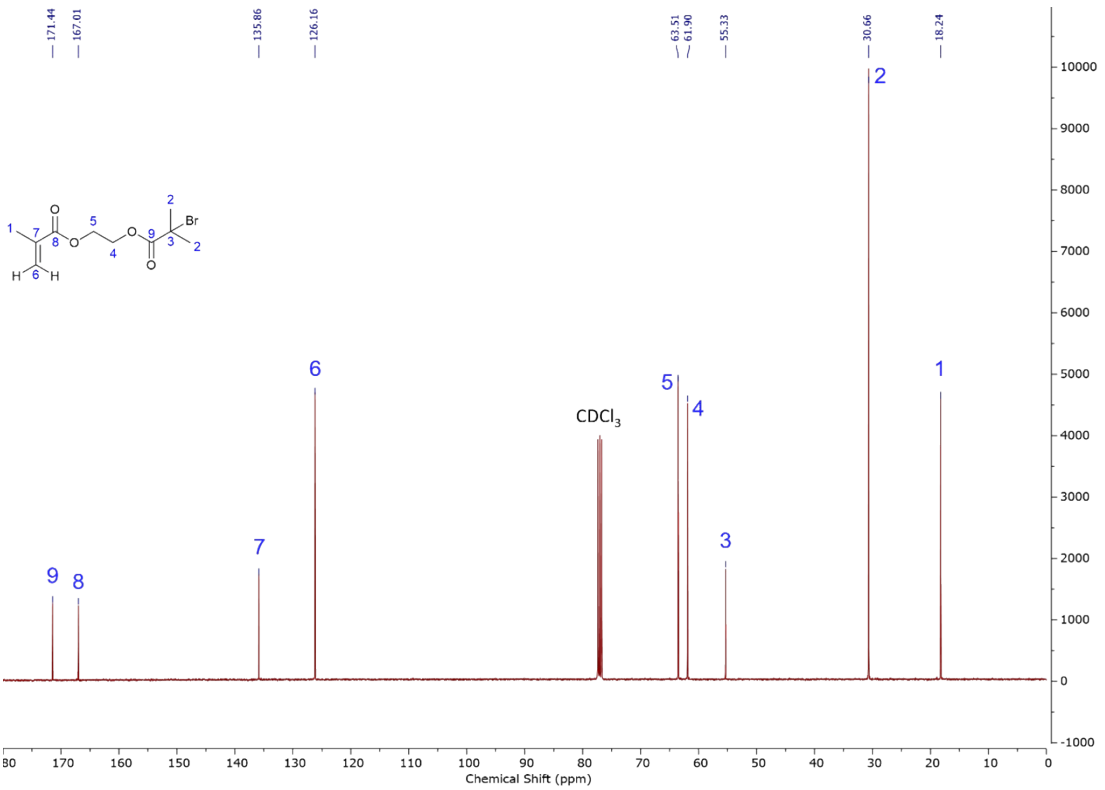


Figure S2: ^{13}C-NMR (400 MHz, $CDCl_3$) spectrum of BBEMA.

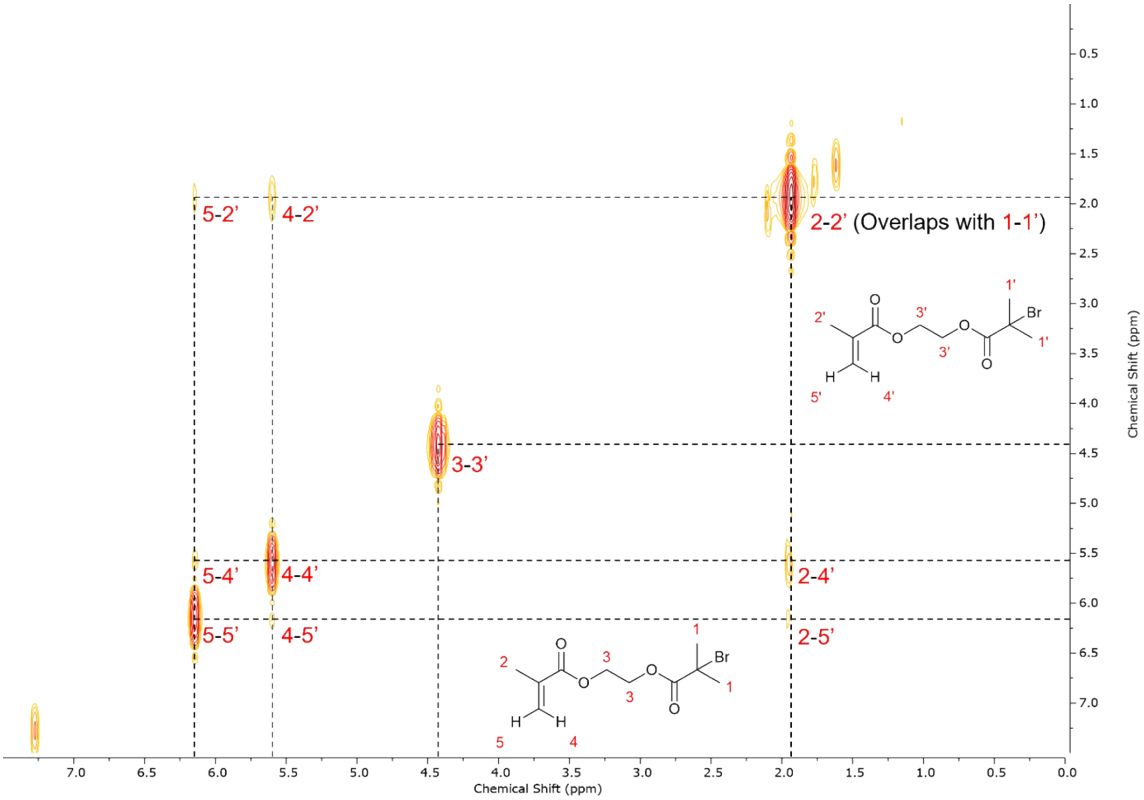


Figure S3: COSY-NMR ($CDCl_3$) spectrum of BBEMA.

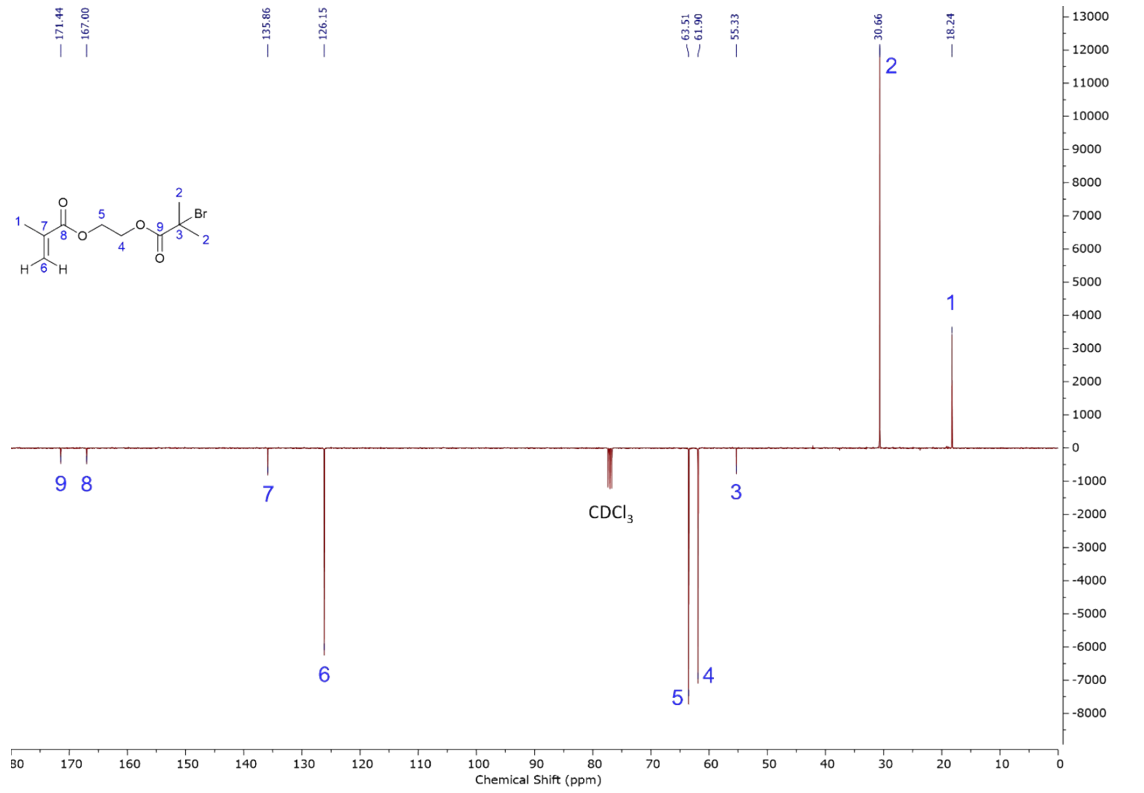


Figure S4: Attached Proton Test (APT) of BBEMA.

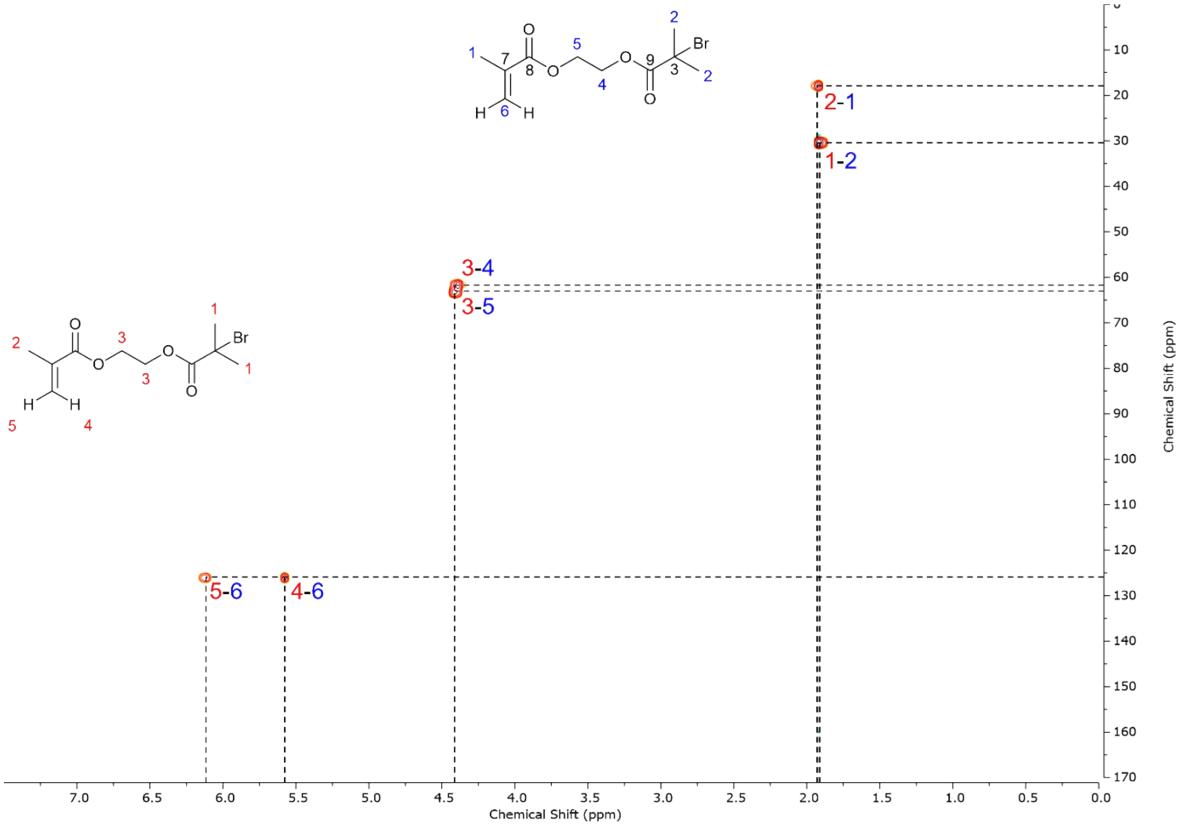


Figure S5: HSQC-NMR ($CDCl_3$) spectrum of BBEMA.

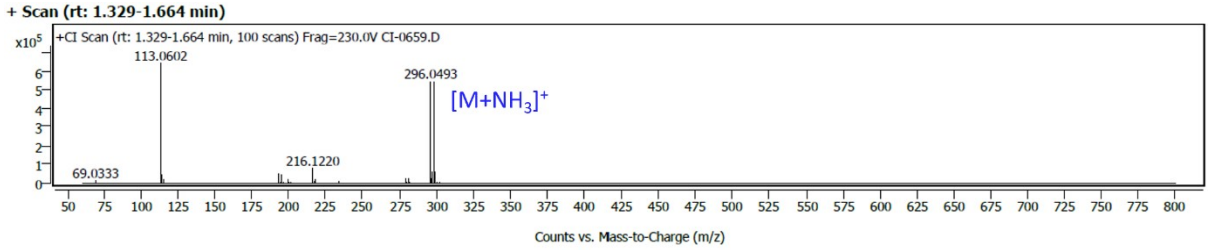


Figure S6: Chemical ionisation mass spectrometry of BBEMA showing the $[M+NH_3]^+$ molecular ion peaks at 296.05 m/z and 298.05 m/z with 1:1 abundance that is consistent with bromine's isotopic pattern.

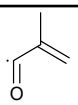
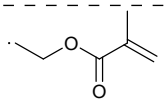
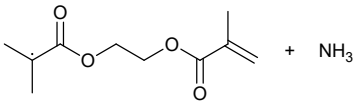
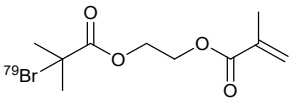
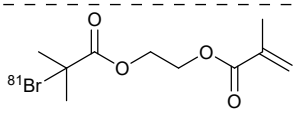
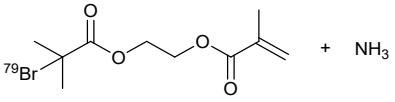
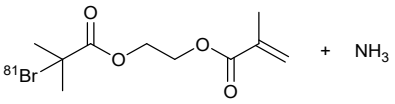
m/z	Abundance (%)	Assignment
69.03	2.23	
113.06	100.00	
216.12	12.95	
279.02	4.00	
281.02	4.00	
296.05	84.56	
298.05	84.54	

Table S2: Assignment of fragments identified in the chemical ionisation mass spectrometry analysis of BBEMA, together with their percentage abundance relative to the base peak. See Figure S6 for the mass spectrum.

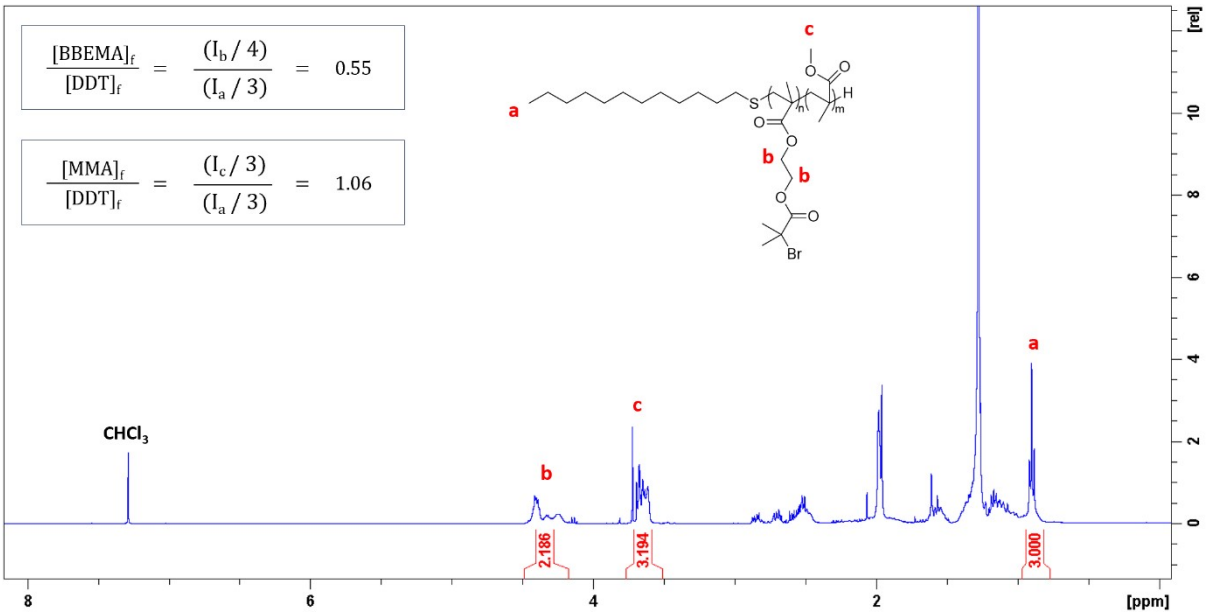


Figure S7: ^{1}H-NMR (400 MHz, $CDCl_3$) of p([DDT-MMA]-*stat*-BBEMA) following the linear co-telomerisation of methyl methacrylate (MMA) and BBEMA in ethyl acetate at 70 °C using dodecanethiol (DDT) as the telogen. The calculations are based on the comparison of integrals of each residue after having normalised the integrals to that of the methyl group (3H) of DDT at 0.88 ppm.

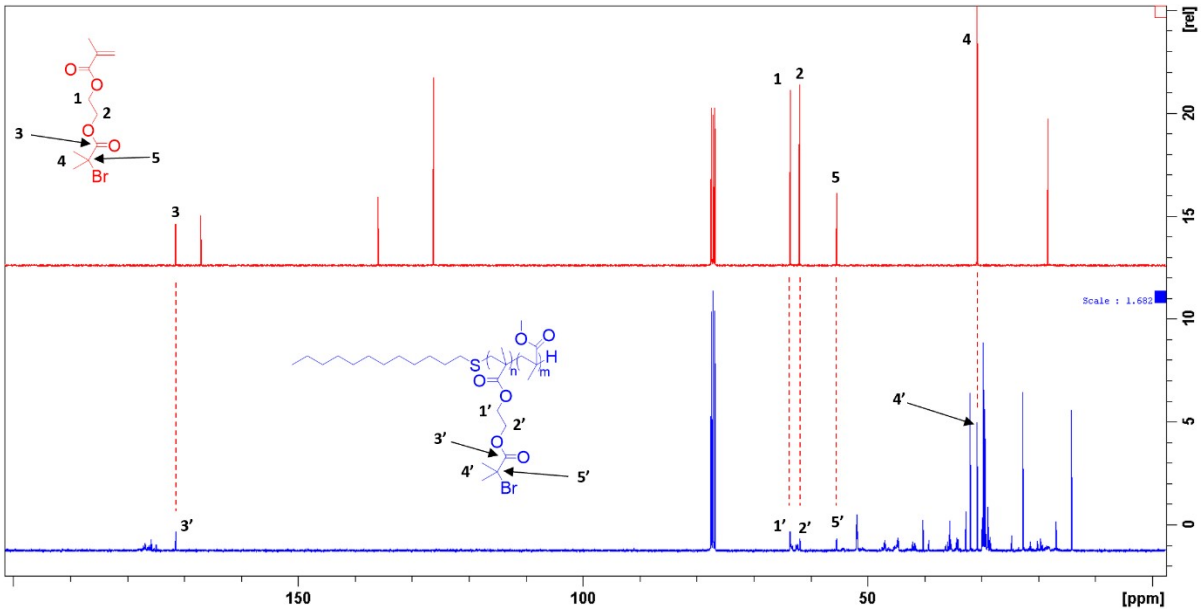


Figure S8: Overlay of ^{13}C-NMR spectra of BBEMA (red) and p([DDT-MMA]-*stat*-BBEMA) (blue) following the linear co-telomerisation of MMA and BBEMA in ethyl acetate at 70 °C using DDT as the telogen. The red dotted lines show the resonances attributed to the BBEMA residues within the linear co-telomer.

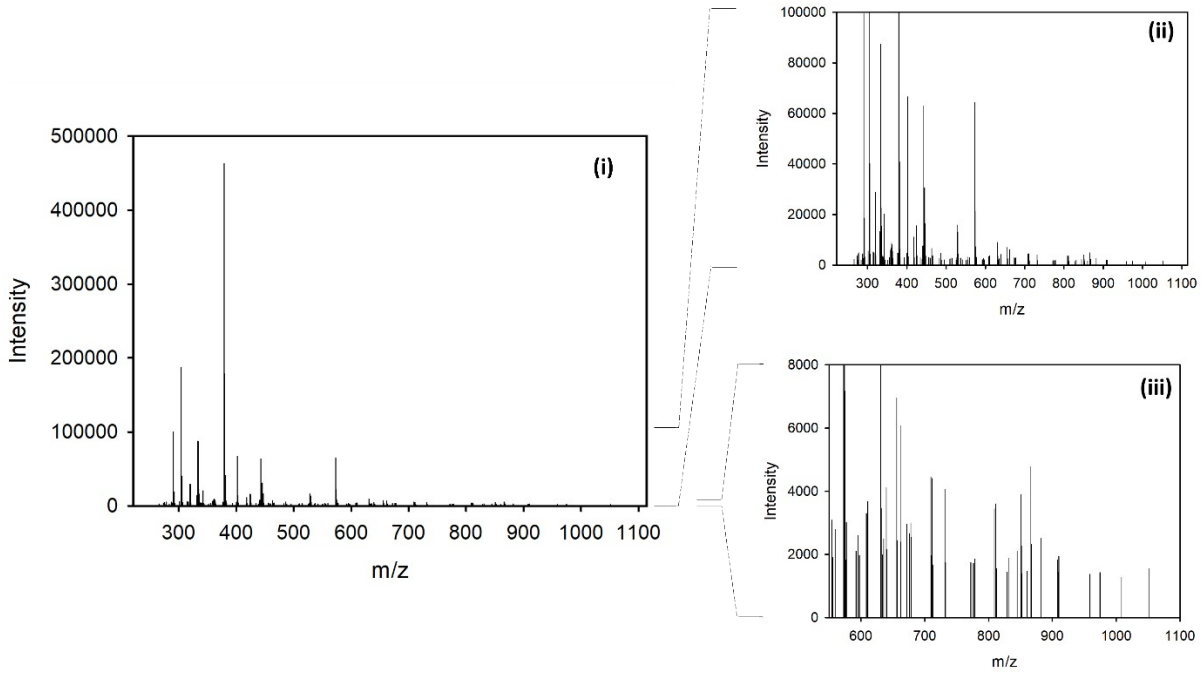


Figure S9: Matrix-assisted laser desorption/ionisation time-of-flight (MALDI TOF) mass spectra of p([DDT-MMA]-*stat*-BBEMA): (i) full spectrum showing all peaks between 200 – 1100 m/z; (ii) spectrum showing all peaks between 200-1100 m/z with magnified y-axis to 0 – 100,000 units; and (iii) spectrum showing peaks between 500-1100 m/z with magnified y-axis to 0 – 8,000 units.

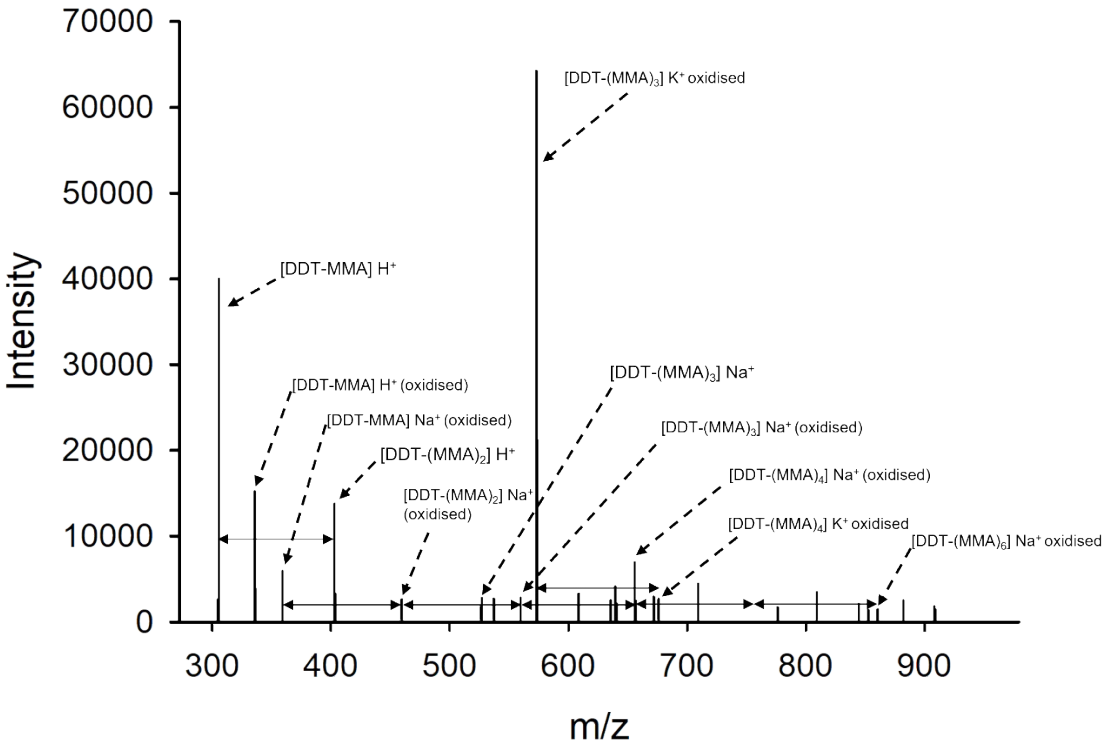
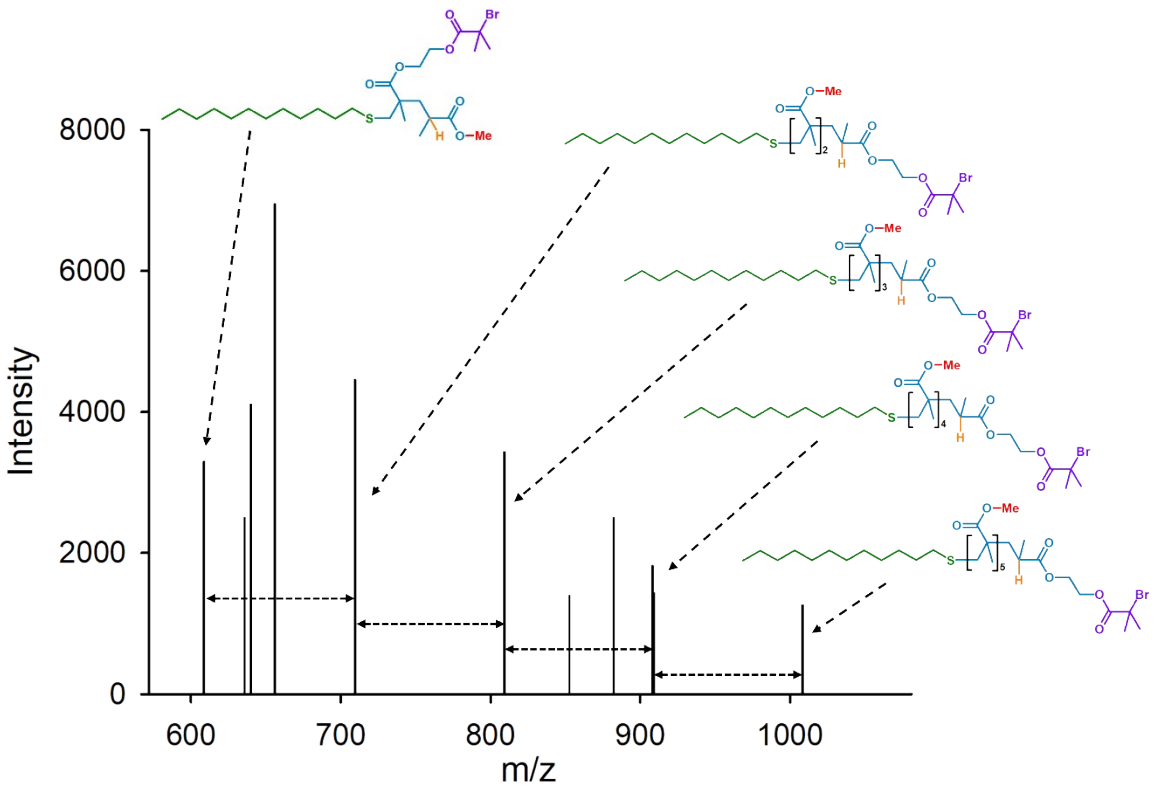


Figure S10: MALDI TOF mass spectrum of p([DDT-MMA]-*stat*-BBEMA) showing DDT-MMA telomers within the sample with different counterions and levels of oxidation of the thioether.



Figures S11: MALDI-TOF mass spectrum of p([DDT-MMA]-*stat*-BBEMA) showing the peaks attributed to various telomer products containing BBEMA residues, all of which are sodium adducts. Unassigned peaks are attributed to oxidised species with varying counterions.

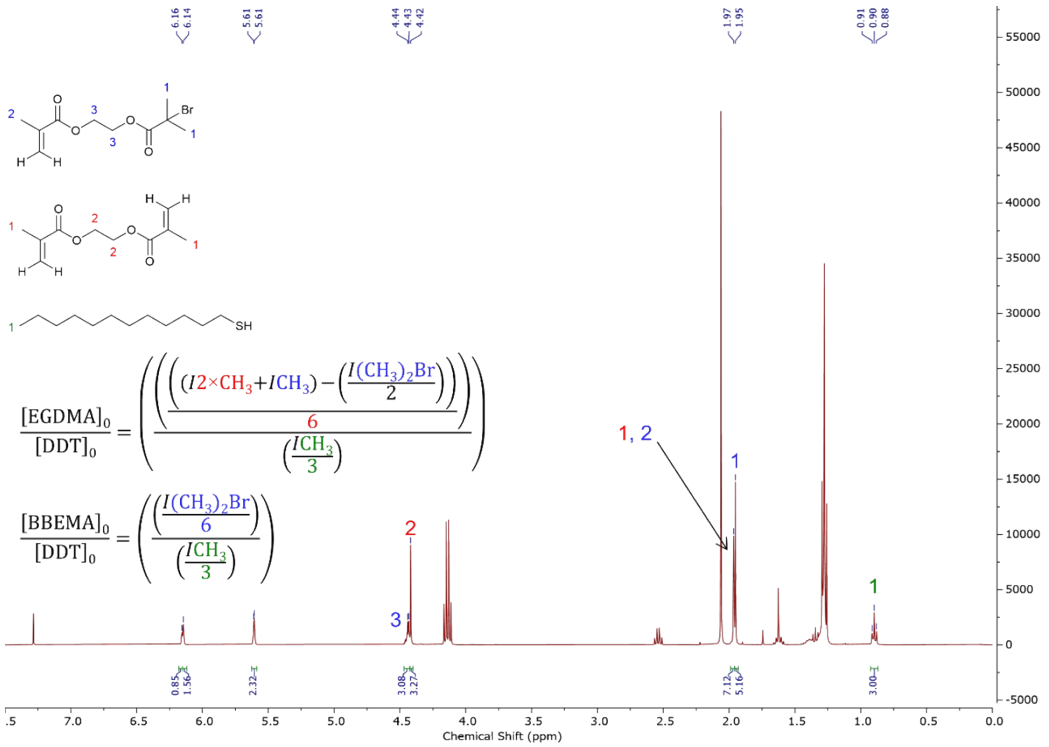


Figure S12: ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of p([DDT-EGDMA]-*stat*-BBEMA) TBRT reaction mixture prior to initiation. The calculations show how the integrals attributed to each residue were used to determine feedstock ratios after having normalised integrals to the methyl group of DDT.

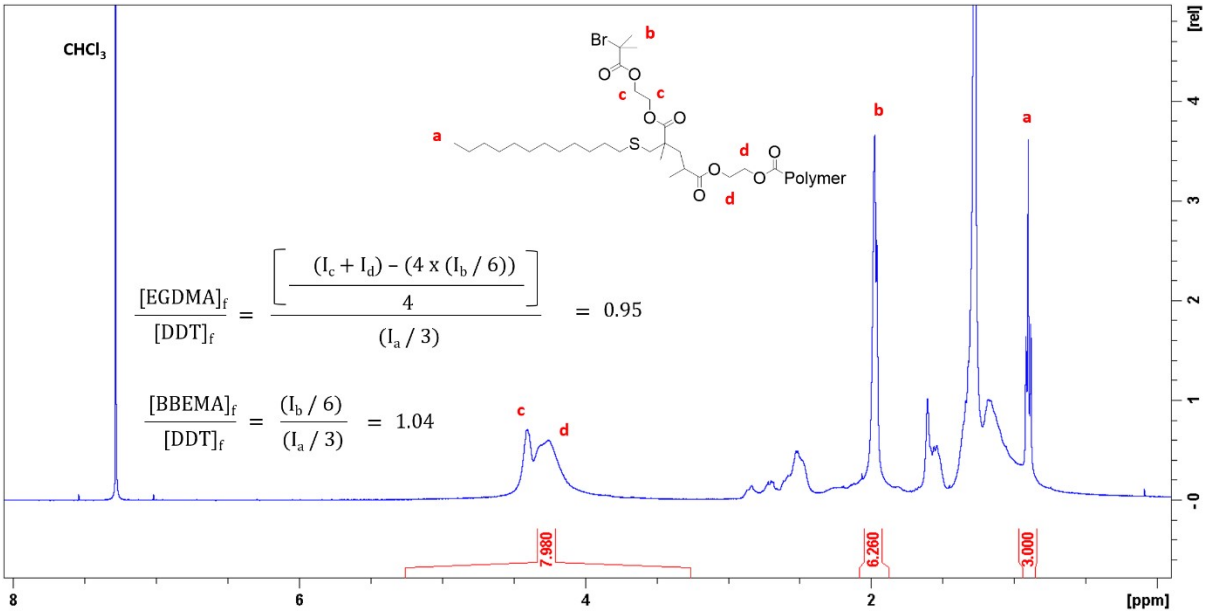


Figure S13: ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of purified p([DDT-EGDMA]-*stat*-BBEMA). The calculations show how the integrals of each residue were used to calculate final compositions after having normalised integrals to the methyl group (3H) of DDT at 0.88 ppm.

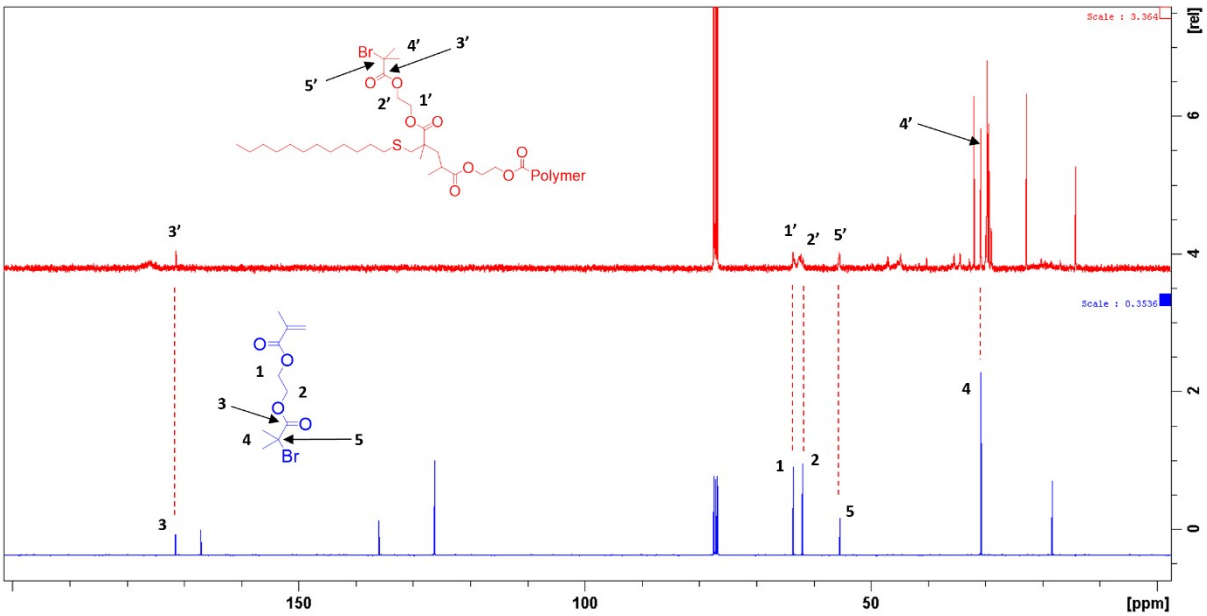


Figure S14: Overlay of ^{13}C-NMR spectra of p([DDT-EGDMA]-*stat*-BBEMA) in red, and BBEMA in blue. The red dotted lines show the resonances attributed to the BBEMA residues within the final TBRT copolymer.

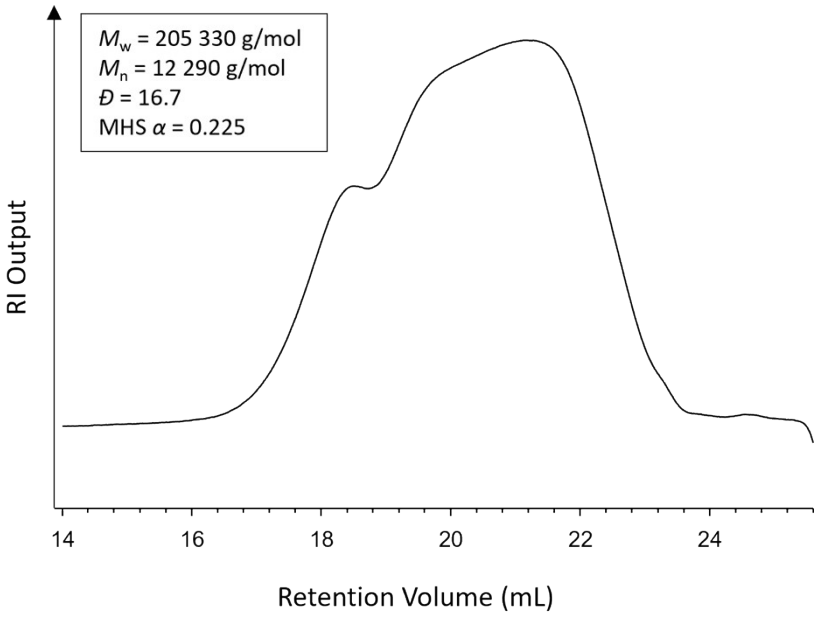


Figure S15: Refractive index (RI) trace of p([DDT-EGDMA]-*stat*-BBEMA) obtained by triple-detection size exclusion chromatography (TD-SEC).

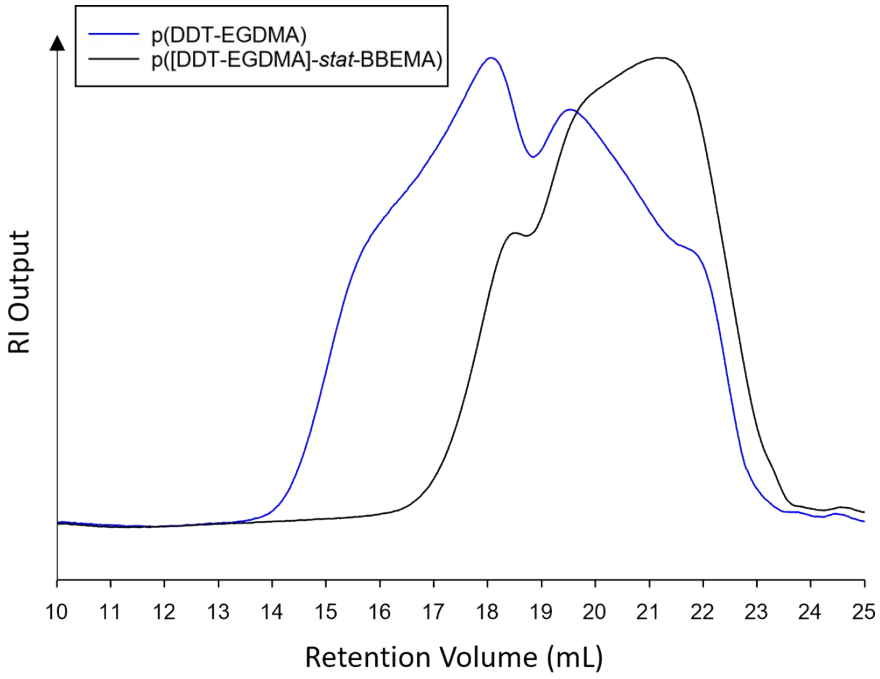


Figure S16: Overlay of RI chromatographic traces obtained by TD-SEC analysis: the p(DDT-EGDMA) and p([DDT-EGDMA]-*stat*-BBEMA) polymers synthesised by TBRT are shown in blue and black, respectively.

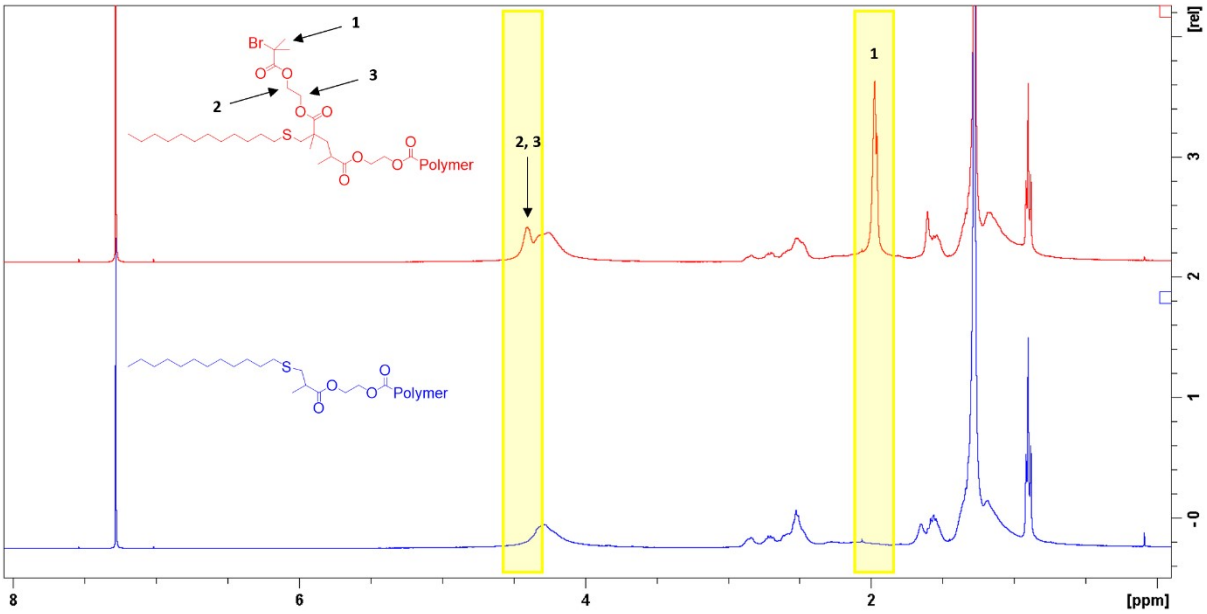


Figure S17: Overlay of ^{1}H-NMR (400 MHz, $CDCl_3$) spectra of p(DDT-EGDMA) (blue trace) and p([DDT-EGDMA]-*stat*-BBEMA) (red trace). The yellow boxes highlight the resonances attributed to the BBEMA residues within the p([DDT-EGDMA]-*stat*-BBEMA) copolymer.

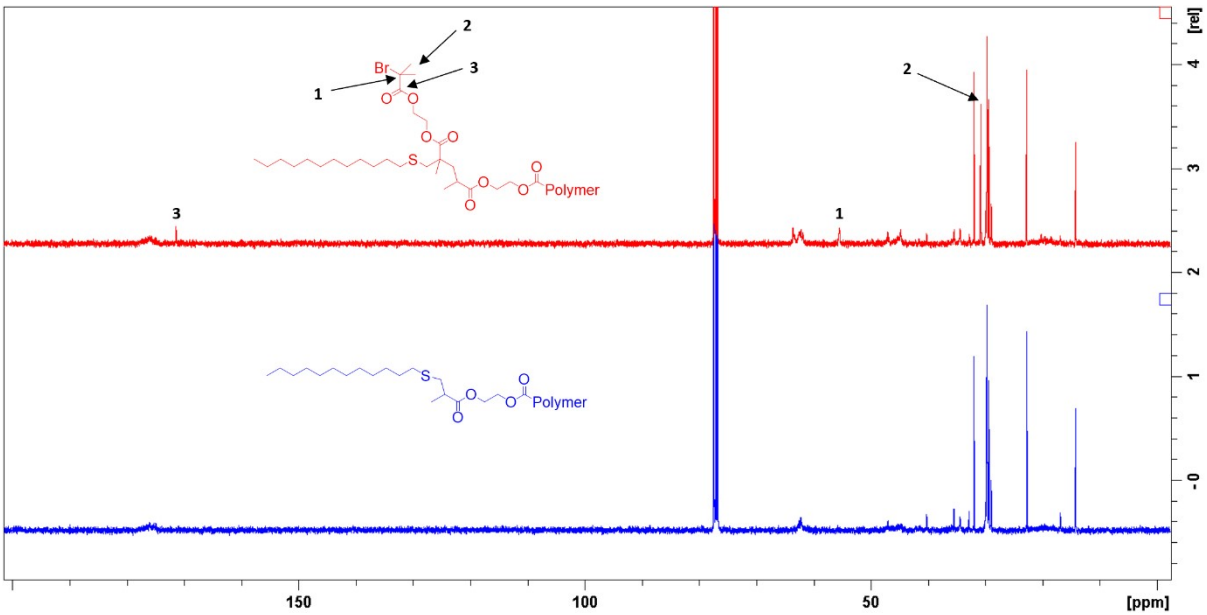


Figure S18: Overlay of ^{13}C-NMR ($CDCl_3$) spectra of p(DDT-EGDMA) (blue trace) and p([DDT-EGDMA]-*stat*-BBEMA) (red trace), with the resonances attributed to the BBEMA residues within the p([DDT-EGDMA]-*stat*-BBEMA) copolymer assigned.

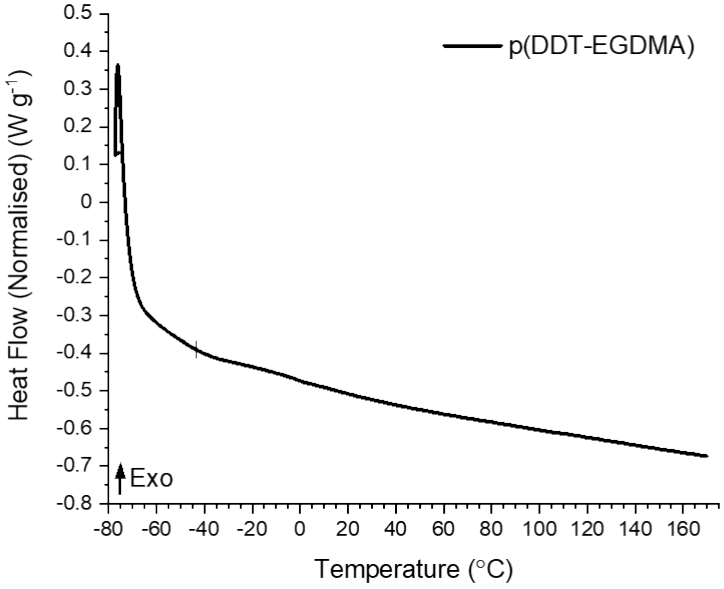


Figure S19: Differential scanning calorimetry (DSC) thermogram of p(DDT-EGDMA).

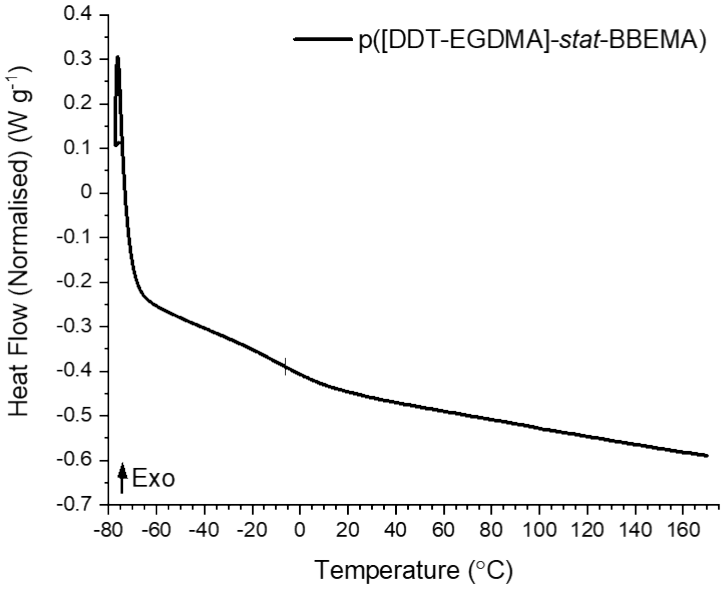


Figure S20: DSC Thermogram of p([DDT-EGDMA]-*stat*-BBEMA).

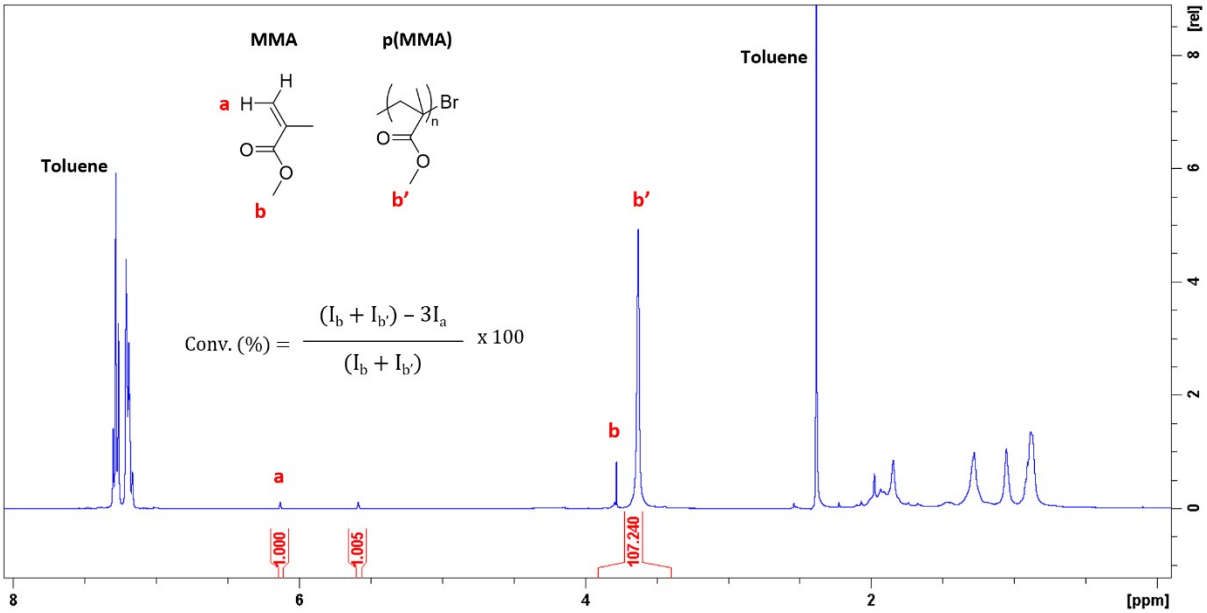


Figure S21: ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of a crude reaction mixture taken from the atom transfer radical polymerisation (ATRP) of MMA using p([DDT-EGDMA]-*stat*-BBEMA) as macro-initiator to yield p([DDT-EGDMA]-*star*-MMA). The equation shows how vinyl conversion was calculated by comparing integrals attributed to monomer residues and residual monomer.

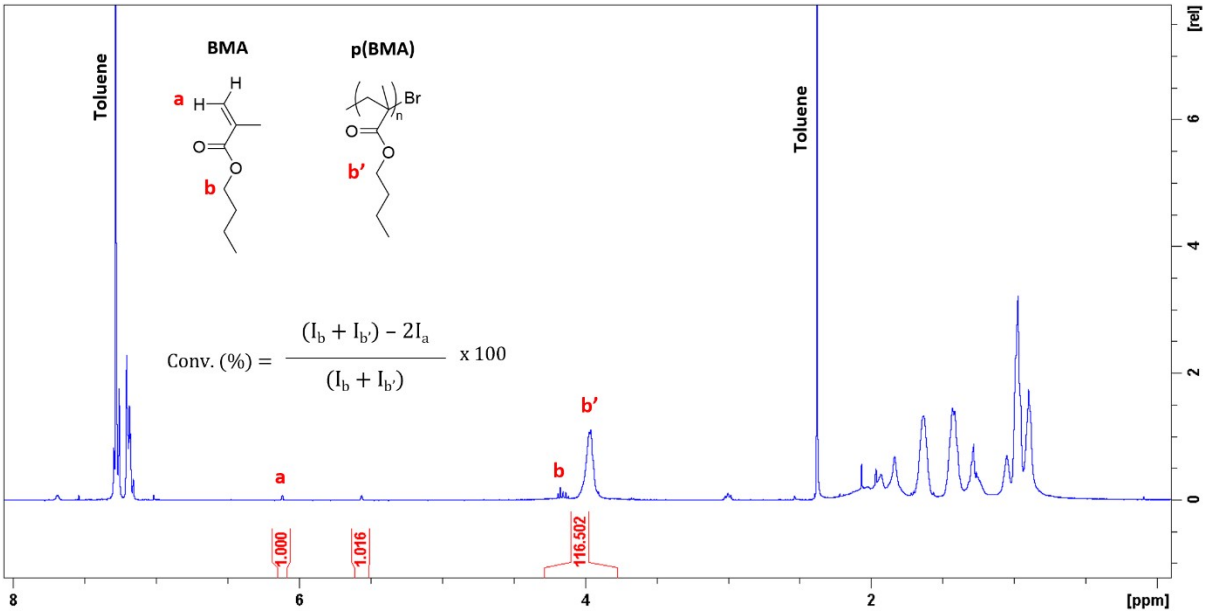


Figure S22: ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of a crude reaction mixture taken from the ATRP of butyl methacrylate (BMA) using p([DDT-EGDMA]-*stat*-BBEMA) as macro-initiator to yield p([DDT-EGDMA]-*star*-BMA). The equation shows how vinyl conversion was calculated by comparing integrals attributed to monomer residues and residual monomer.

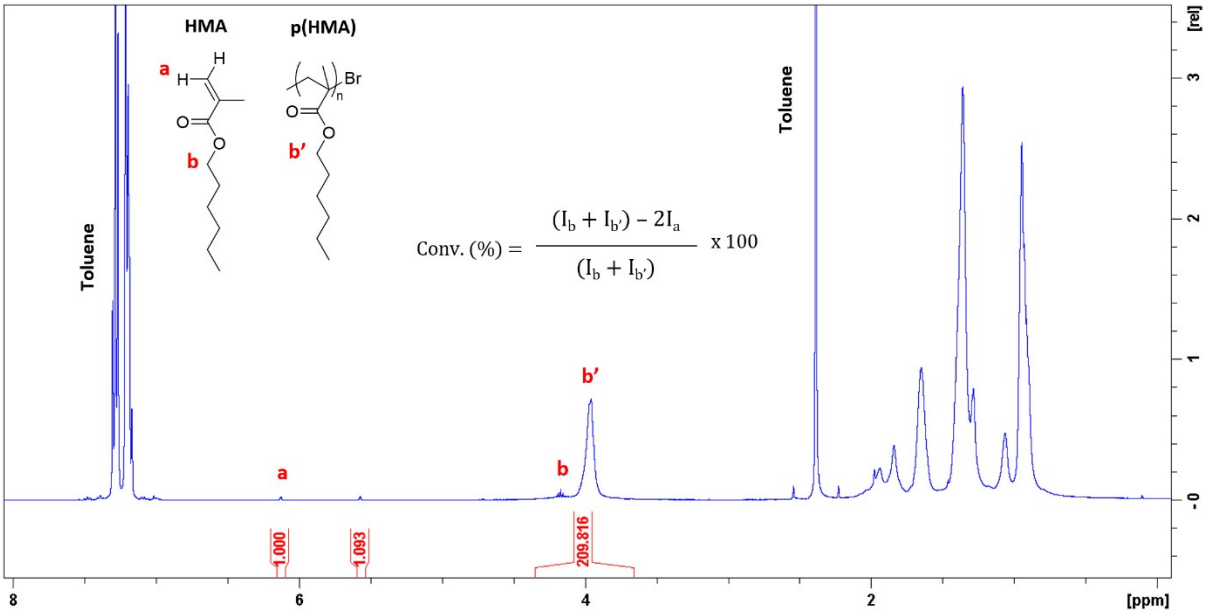


Figure S23: ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of a crude reaction mixture taken from the ATRP of hexyl methacrylate (HMA) using p([DDT-EGDMA]-*stat*-BBEMA) as macro-initiator to yield p([DDT-EGDMA]-*star*-HMA). The equation shows how vinyl conversion was calculated by comparing integrals attributed to monomer residues and residual monomer.

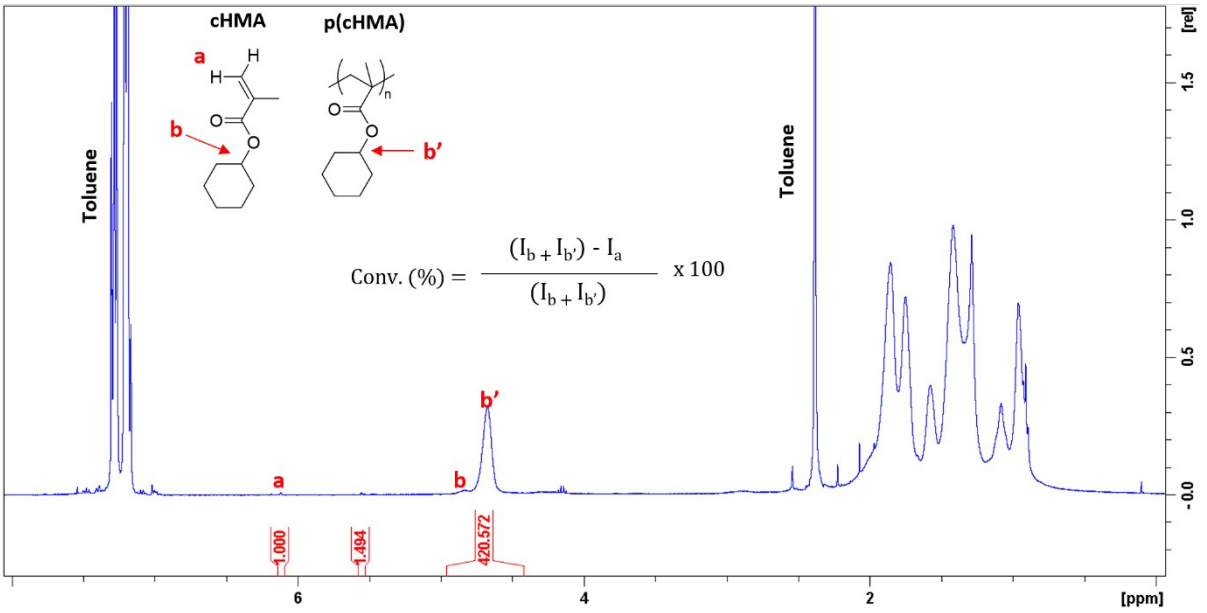


Figure S24: ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of a crude reaction mixture taken from the ATRP of cyclohexyl methacrylate (cHMA) using p([DDT-EGDMA]-*stat*-BBEMA) as macro-initiator to yield p([DDT-EGDMA]-*star*-cHMA). The equation shows how vinyl conversion was calculated by comparing integrals attributed to monomer residues and residual monomer.

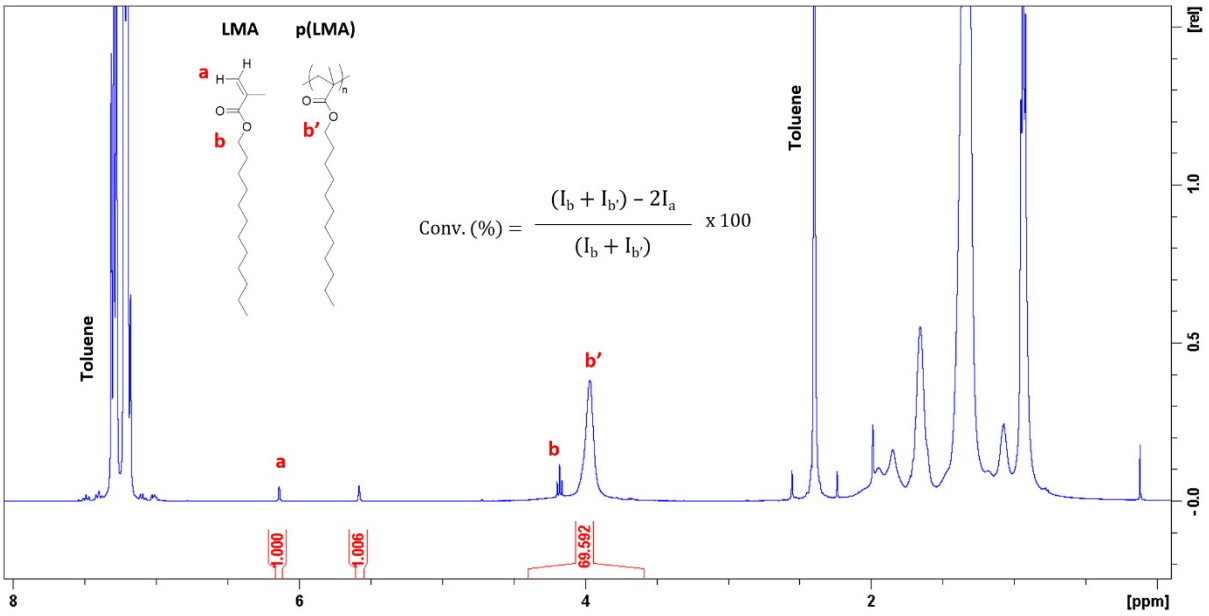


Figure S25: ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of a crude reaction mixture taken from the ATRP of lauryl methacrylate (LMA) using p([DDT-EGDMA]-*stat*-BBEMA) as macro-initiator to yield p([DDT-EGDMA]-*star*-LMA). The equation shows how vinyl conversion was calculated by comparing integrals attributed to monomer residues and residual monomer.

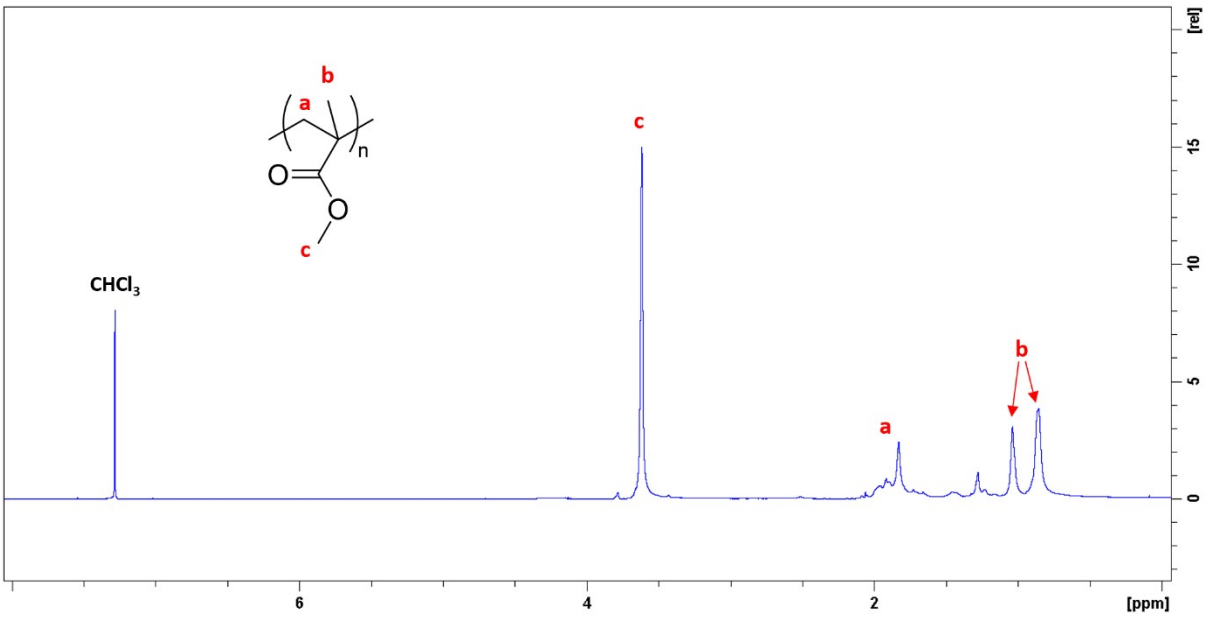


Figure S26: ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of p([DDT-EGDMA]-*star*-MMA) following purification.

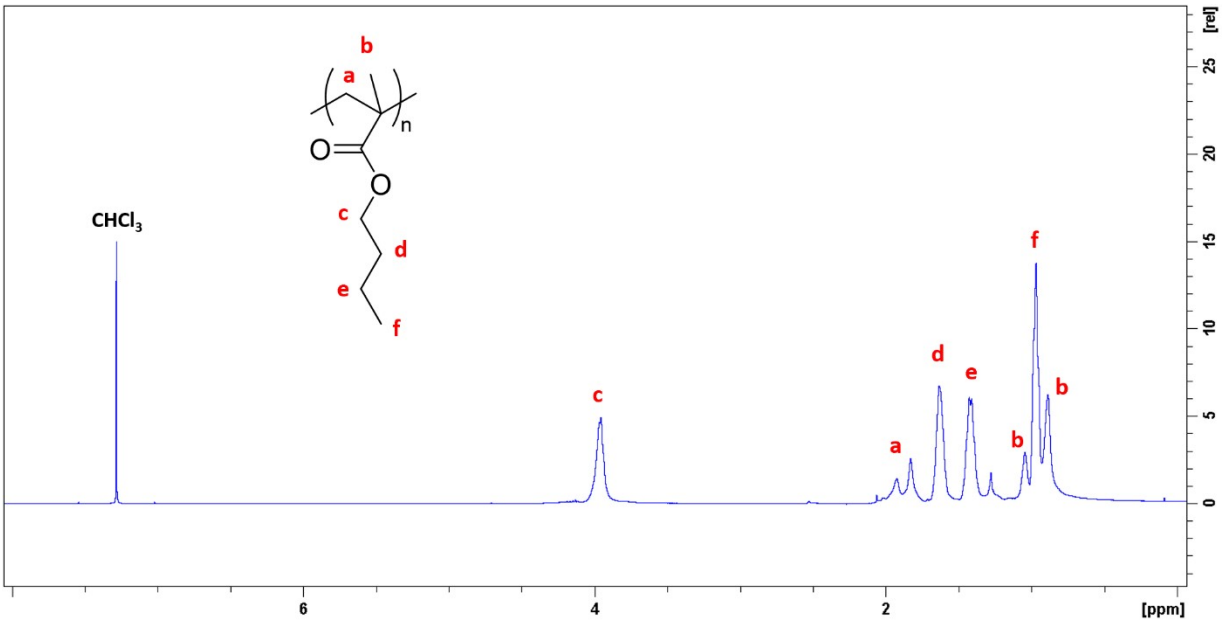


Figure S27: ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of p([DDT-EGDMA]-*star*-BMA) following purification.

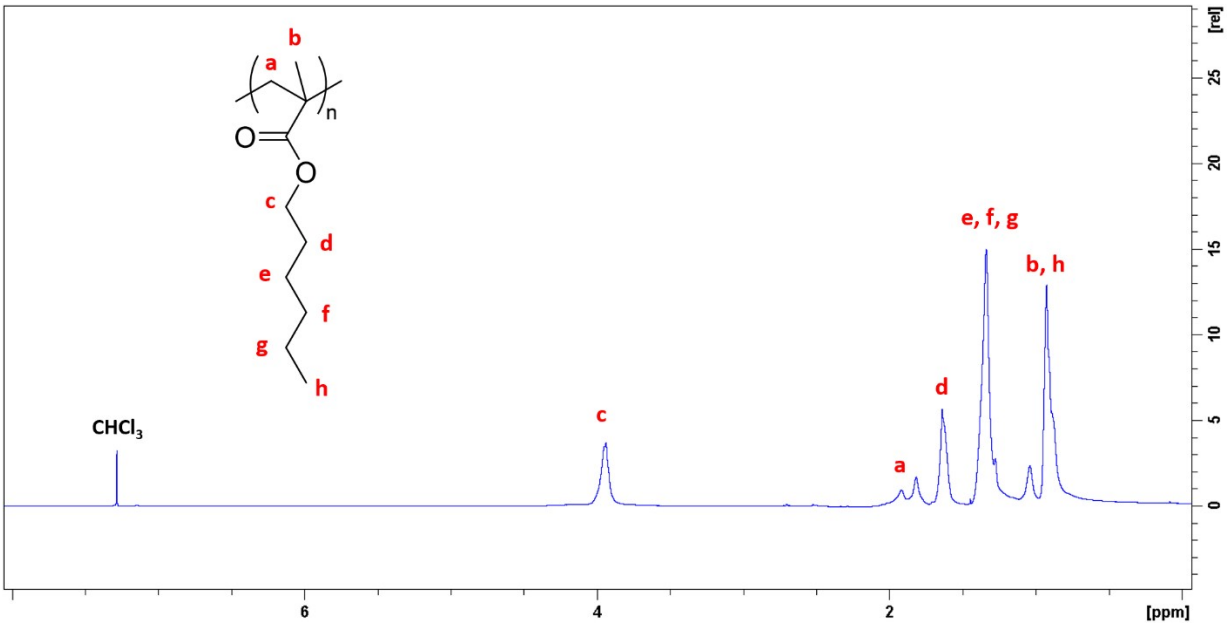


Figure S28: ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of p([DDT-EGDMA]-*star*-HMA) following purification.

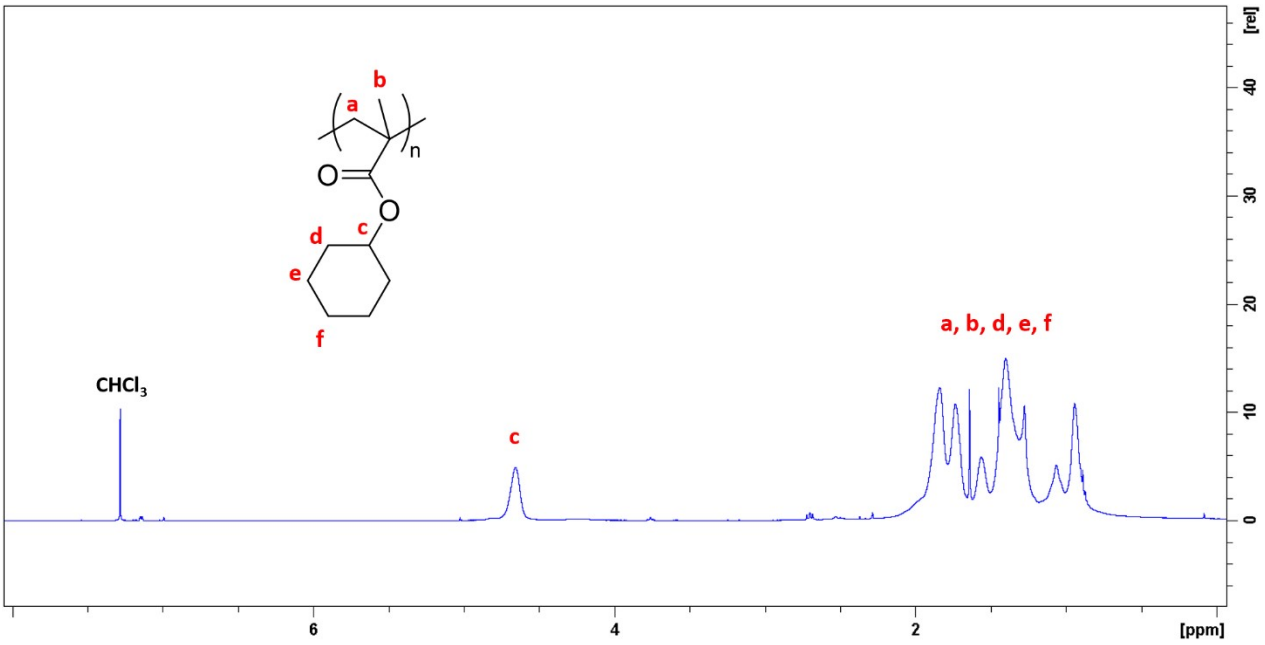


Figure S29: ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of p([DDT-EGDMA]-*star*-cHMA) following purification.

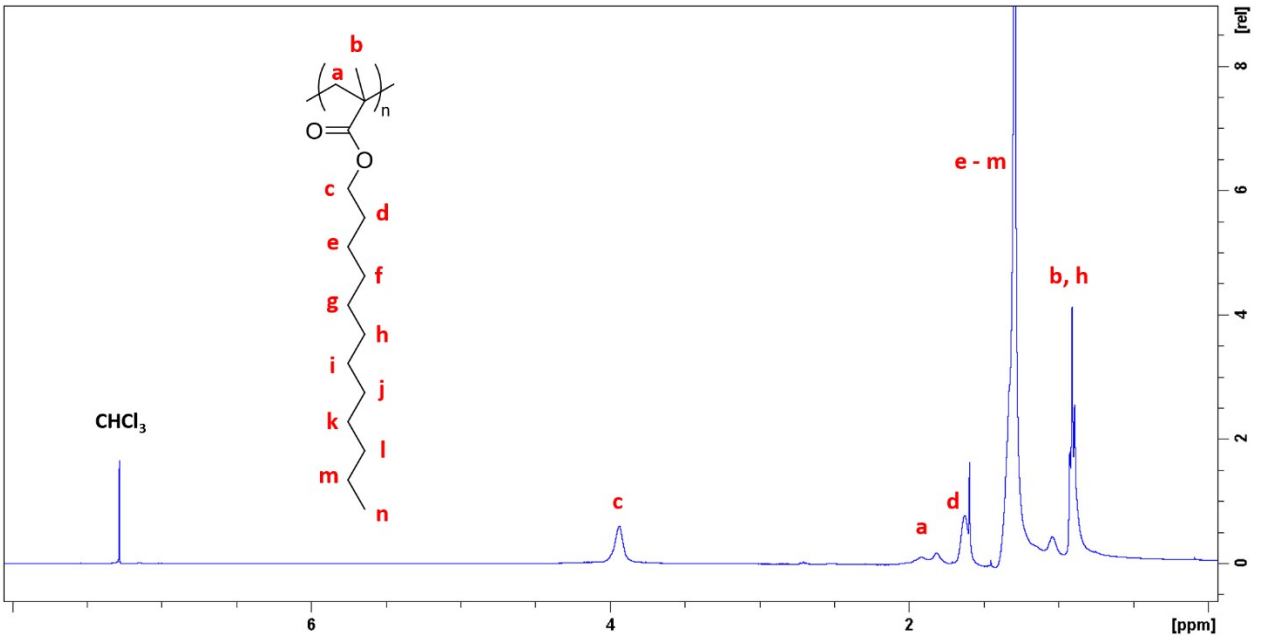


Figure S30: ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of p([DDT-EGDMA]-*star*-LMA) following purification.

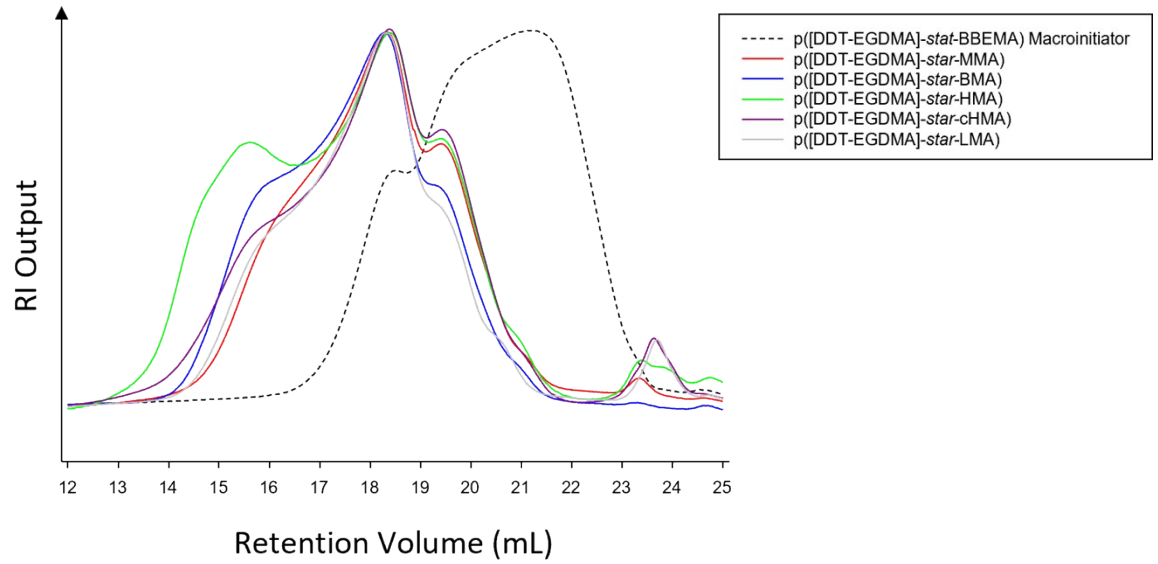


Figure S31: Overlay of RI chromatographic traces obtained by TD-SEC analysis. The trace for the p([DDT-EGDMA]-*stat*-BBEMA) macro-initiator is shown by the black dotted line. The p([DDT-EGDMA]-*star*-XXX) polymers are shown by the solid lines: p([DDT-EGDMA]-*star*-MMA) (red), p([DDT-EGDMA]-*star*-BMA) (blue), p([DDT-EGDMA]-*star*-HMA) (green), p([DDT-EGDMA]-*star*-cHMA) (purple), and p([DDT-EGDMA]-*star*-LMA) (grey).

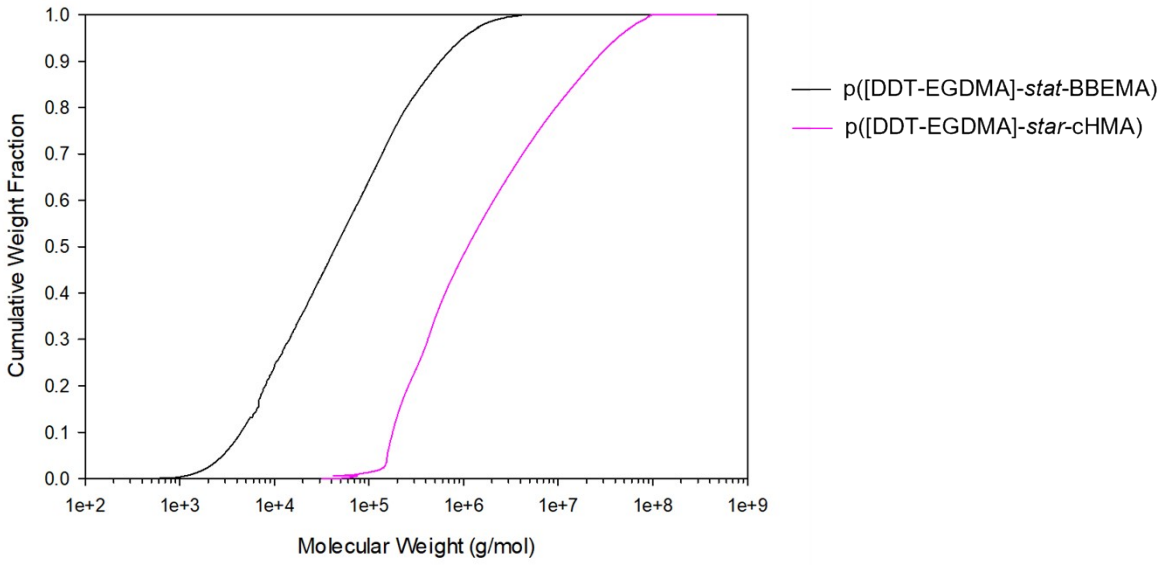


Figure S32: An overlay of plots of the cumulative weight fraction as a function of molecular weight following TD-SEC analysis. The trace for the p([DDT-EGDMA]-*stat*-BBEMA) macro-initiator is shown by the black solid line. The p([DDT-EGDMA]-*star*-cHMA) is shown by the pink solid line.

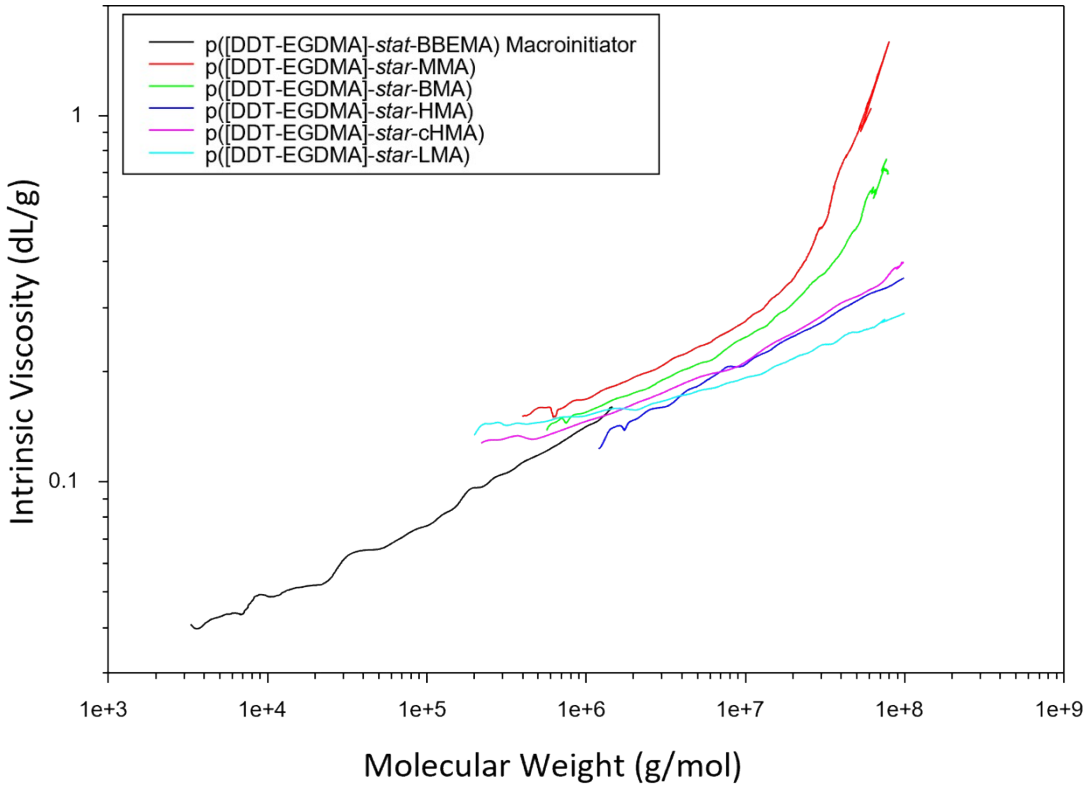


Figure S33: An overlay of Mark-Houwink-Sakurada plots following TD-SEC analysis. The trace for the p([DDT-EGDMA]-*stat*-BBEMA) macro-initiator is shown by the black solid line. The p([DDT-EGDMA]-*star*-XXX) polymers are shown by the following: p([DDT-EGDMA]-*star*-MMA) (red), p([DDT-EGDMA]-*star*-BMA) (green), p([DDT-EGDMA]-*star*-HMA) (blue), p([DDT-EGDMA]-*star*-cHMA) (pink), and p([DDT-EGDMA]-*star*-LMA) (turquoise).

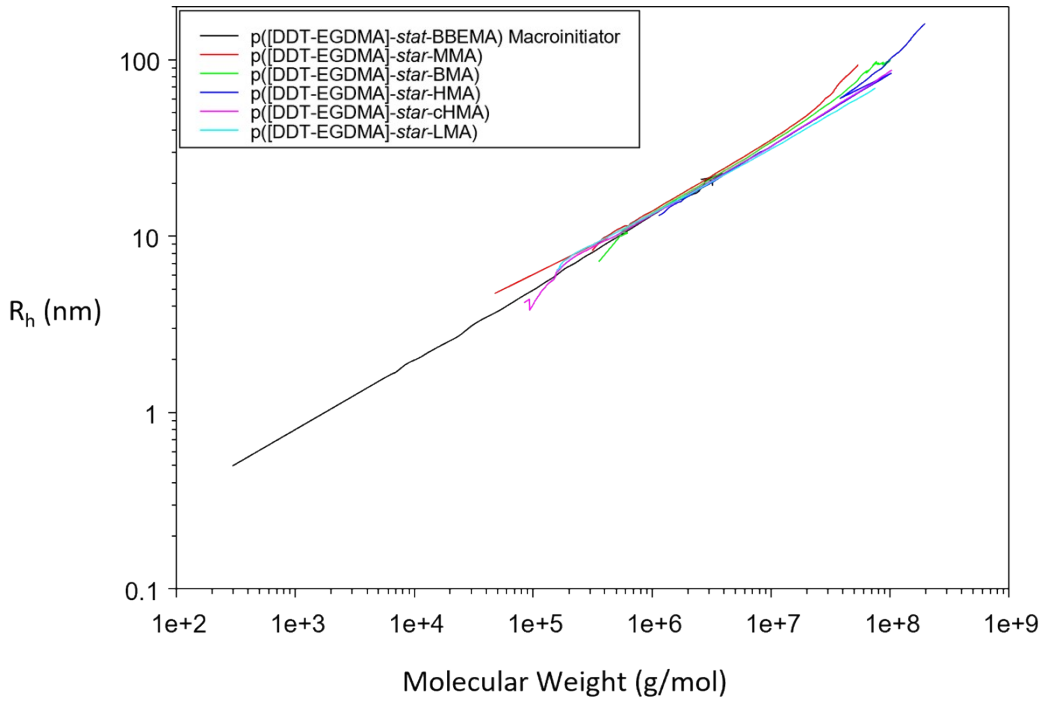


Figure S34: An overlay of plots of the hydrodynamic radii as a function of molecular weight following TD-SEC analysis. The trace for the p([DDT-EGDMA]-*stat*-BBEMA) macro-initiator is shown by the black solid line. The p([DDT-EGDMA]-*star*-XXX) polymers are shown by the following: p([DDT-EGDMA]-*star*-MMA) (red), p([DDT-EGDMA]-*star*-BMA) (green), p([DDT-EGDMA]-*star*-HMA) (blue), p([DDT-EGDMA]-*star*-cHMA) (pink), and p([DDT-EGDMA]-*star*-LMA) (turquoise).

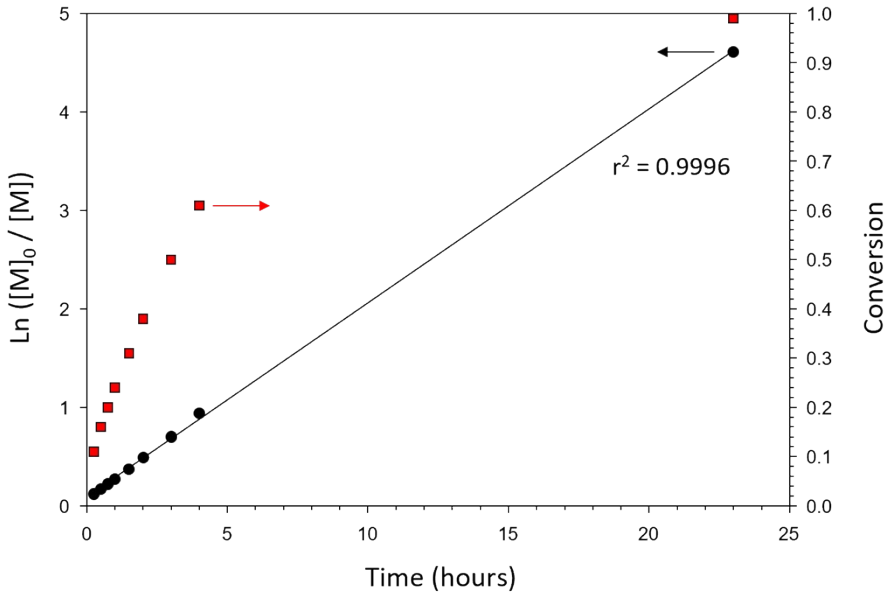


Figure S35: Kinetic studies of the ATRP of LMA using p([DDT-EGDMA]-*stat*-BBEMA) as macro-initiator: vinyl conversion vs. reaction time (red squares), and the corresponding semi-logarithmic plot (black circles) with linear regression analysis (black line) investigating the consumption of monomer over time.

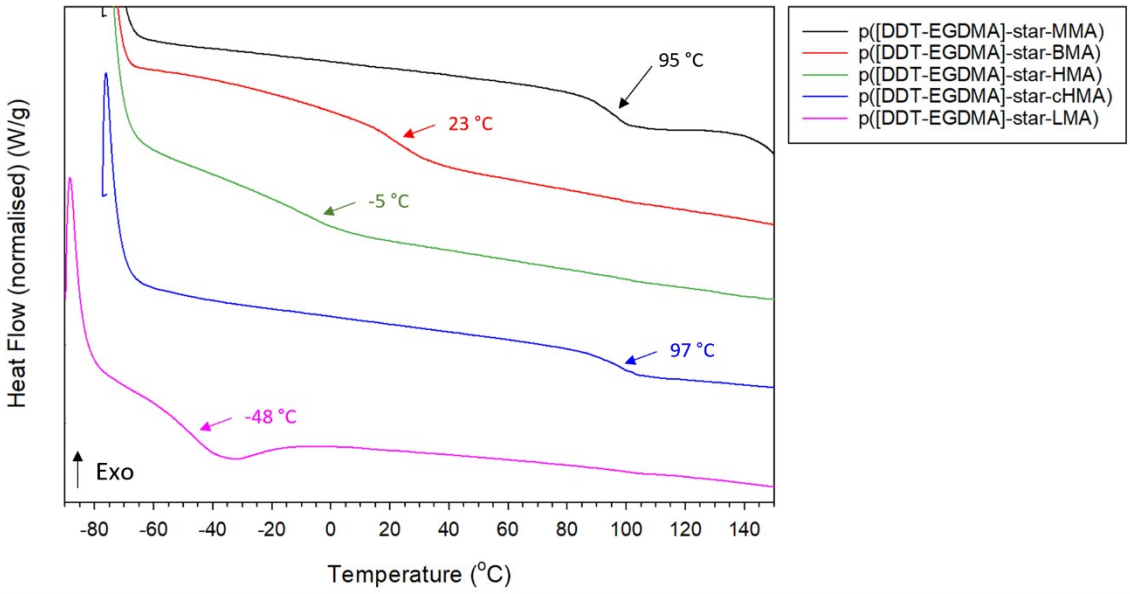


Figure S36: An overlay of DSC thermograms of p([DDT-EGDMA]-*star*-MMA) (black), p([DDT-EGDMA-*star*-BMA) (red), p([DDT-EGDMA]-*star*-HMA) (green), p([DDT-EGDMA]-*star*-cHMA) (blue), and p([DDT-EGDMA]-*star*-LMA) (pink), each annotated with their T_g values determined by analysing the mid-point of the transitions.