Supporting Information

In Situ Xanthate Deprotection to Generate Thiol Chain Transfer Agents for Conventional Free Radical Linear and Branched Vinyl Polymerisation

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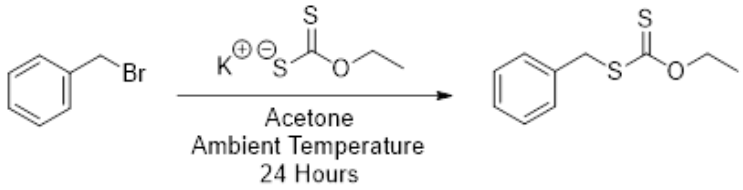
Materials & Characterisation

Azobisisobutyronitrile (98 %), triethyl amine (TEA, > 99 %) Benzyl bromide (98 %), benzyl mercaptan (99 %), *n*-butyl methacrylate (99 %), ethylene glycol dimethacrylate (98 %), chloroform-d ($CDCl_3$, 99.8 atom %), toluene-d_8 (99 atom %) and anhydrous toluene (99.8 %) were purchased from Sigma Aldrich. Acetone (analytical grade), Toluene (analytical grade), Hexane (analytical grade), diethyl ether (analytical grade), ethyl acetate (analytical grade) tetrahydrofuran (THF, HPLC grade) and methanol (analytical grade) were purchased from Fisher Scientific. Potassium ethyl xanthogenate (98 %) and *n*-butyl amine (99 %) were purchased from Alfa Aesar. All goods were used as received.

Nuclear magnetic resonance (NMR) spectrometry was conducted using a Bruker Avance spectrometer and was measured at 400 MHz and 100 MHz for ^1H and ^{13}C nuclei, respectively. NMR spectra were obtained in $CDCl_3$ and toluene-d_8 containing tetramethylsilane (TMS) which was used as an internal standard for both ^1H and ^{13}C spectra. Chemical shifts (δ) are reported in parts per million (ppm). Ultraviolet-visible spectroscopy (UV-Vis) was conducted using a Thermo Scientific NanoDrop 2000c spectrometer monitoring the absorption at λ max = 287 nm operating in cuvette mode. The instrument was calibrated by measuring background absorbance of toluene before UV-Vis measurements were taken. Triple detection gel permeation chromatography (GPC) was performed using a Malvern Viscotek instrument equipped with a GPCmax VE2001 auto-sampler, two Viscotek T6000 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 and a flow-rate of 1 mL min^{-1}.

Experimental

Synthesis of *S*-benzyl *O*-ethyl carbonodithioate (BzXan)



Potassium ethyl xanthogenate (9.37 g, 58.5 mmol) and acetone (100 mL) were added to a round bottom flask equipped with a magnetic stirrer bar. Benzyl bromide (5.00 g, 29.2 mmol) was dissolved in acetone (50 mL) and the solution was then added dropwise to the round bottom flask *via* a pressure equalising dropping funnel at ambient temperature. After 24h acetone was removed *in vacuo*, the crude product extracted with diethyl ether (3 x 100 mL) and dried *in vacuo*. The product was purified by silica gel column chromatography using hexane as the mobile phase (R_f = 0.20) to yield S-benzyl O-ethyl carbondithioate (BzXan) as a yellow oil (4.95 g, 78%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.32 (m, 5H), 4.63 (q, 2H), 4.35 (s, 2H), 1.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 214.03, 135.76, 129.13, 128.67, 127.61, 70.10, 40.48, 13.85. m/z (ES MS) 212.25 $[M^+H]^+$, m/z required 213.03 $[M^+H]^+$. Found, C, 56.84; H, 5.63 %. $C_{10}H_{12}OS_2$ requires, C, 56.57; H, 5.70; O, 7.54; S, 30.20 %.

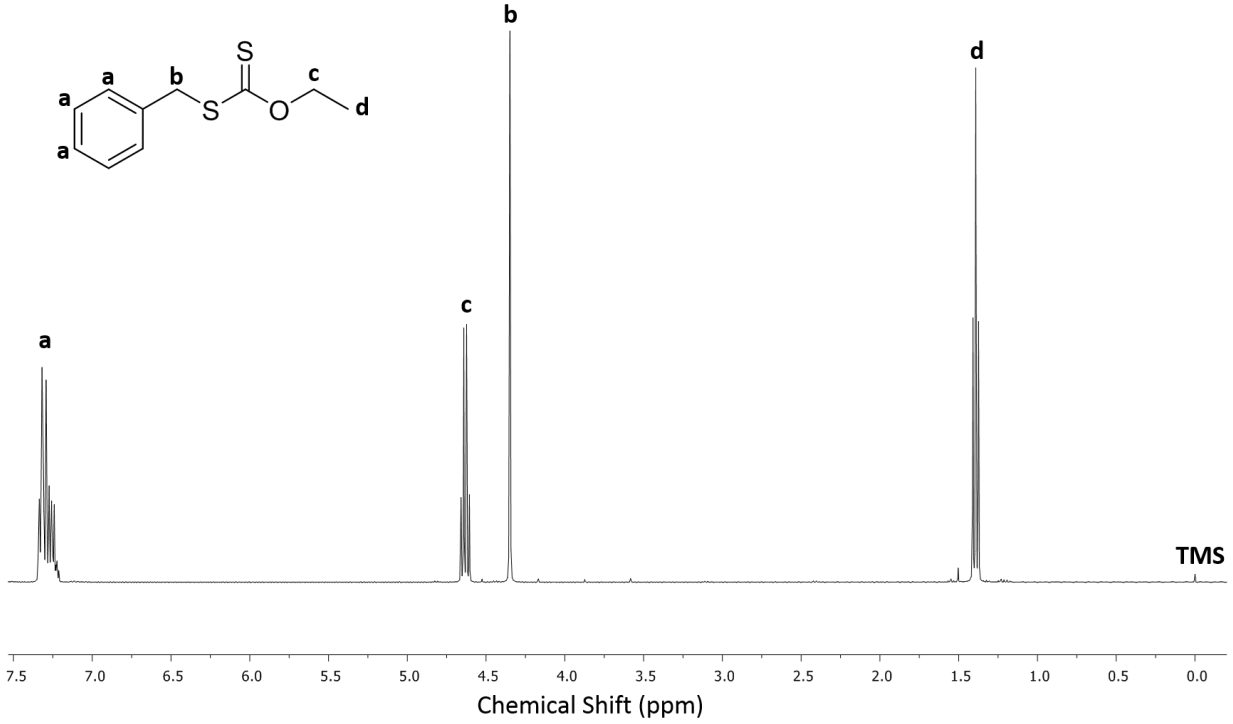


Figure S1 – ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of *S*-benzyl *O*-ethyl carbonodithioate.

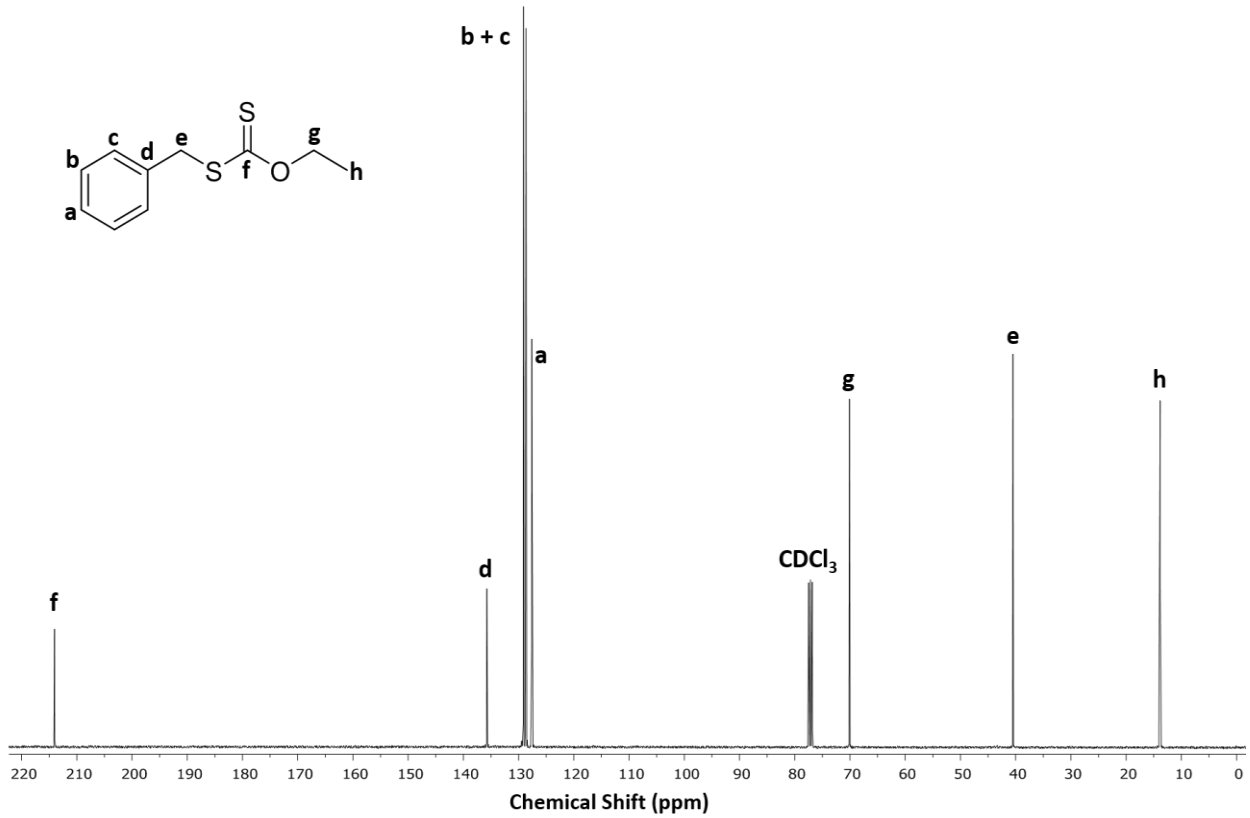


Figure S2 – ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of *S*-benzyl *O*-ethyl carbonodithioate.

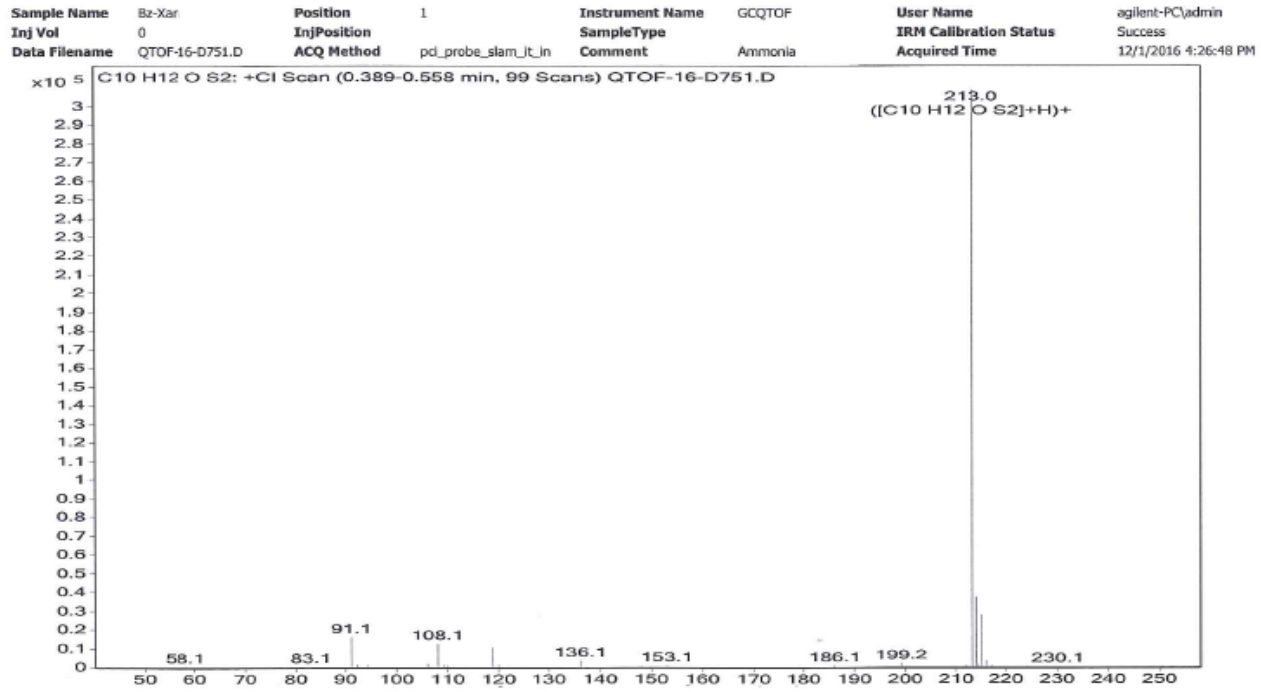
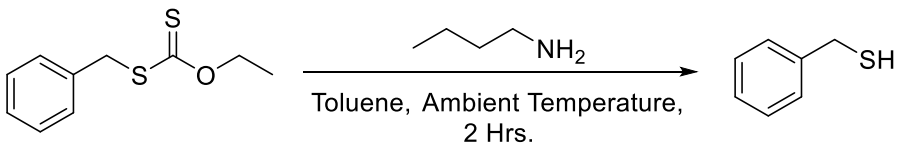


Figure S3 – Chemical ionisation Mass Spectrum of *S*-benzyl *O*-ethyl carbonodithioate

Model Study of Xanthate Deprotection



Benzyl xanthate (2.00 g, 9.40 mmol) and anhydrous toluene (5.00 mL) were added to a round bottom flask equipped with a magnetic stirrer bar. *n*-butyl amine (1.13 mL, 11.3 mmol) was added and the reaction was allowed to proceed at ambient temperature. After 2h the reaction mixture was dried *in-vacuo* and the crude product was purified by silica gel column chromatography using hexane as the mobile phase (R_f = 0.26). The fractions were collected and dried *in-vacuo* at 40 ° C and the product was obtained as a clear oil (910 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61-6.97 (m, 5H), 3.74 (d, 2H), 1.75 (t, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.2, 128.8, 128.1, 127.1, 29.1. m/z

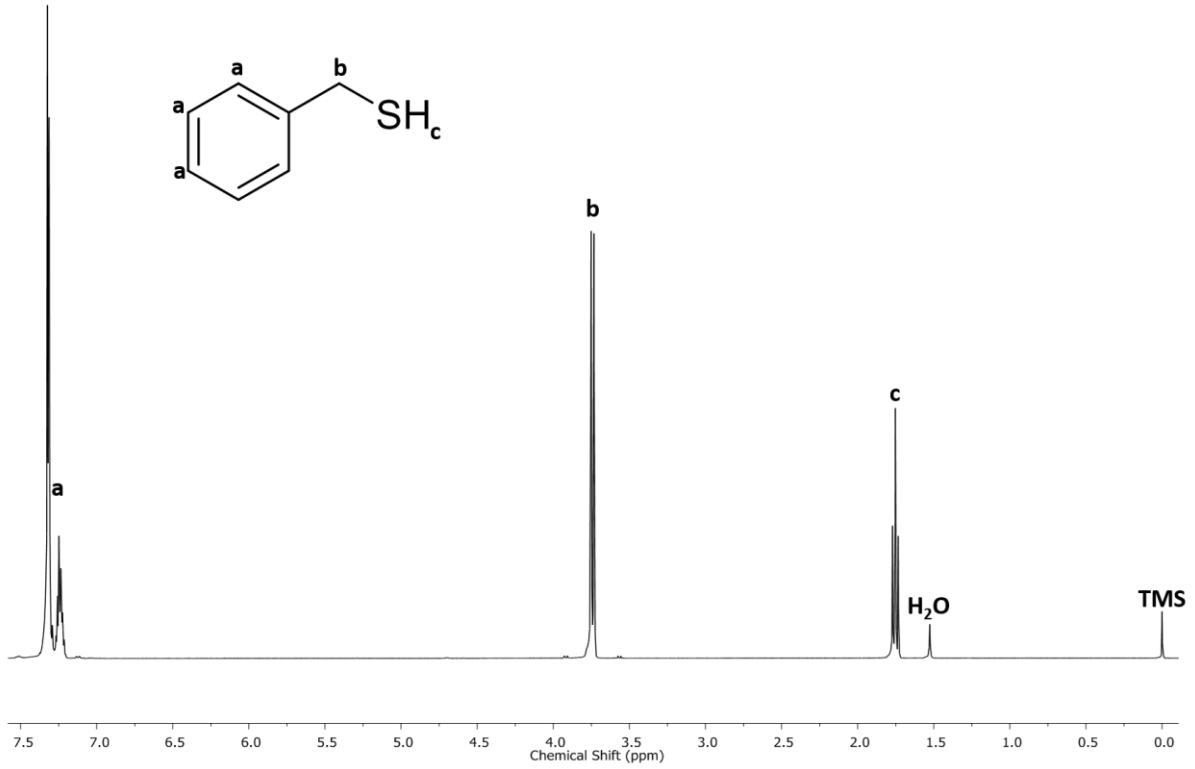


Figure S4 – ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of benzyl mercaptan.

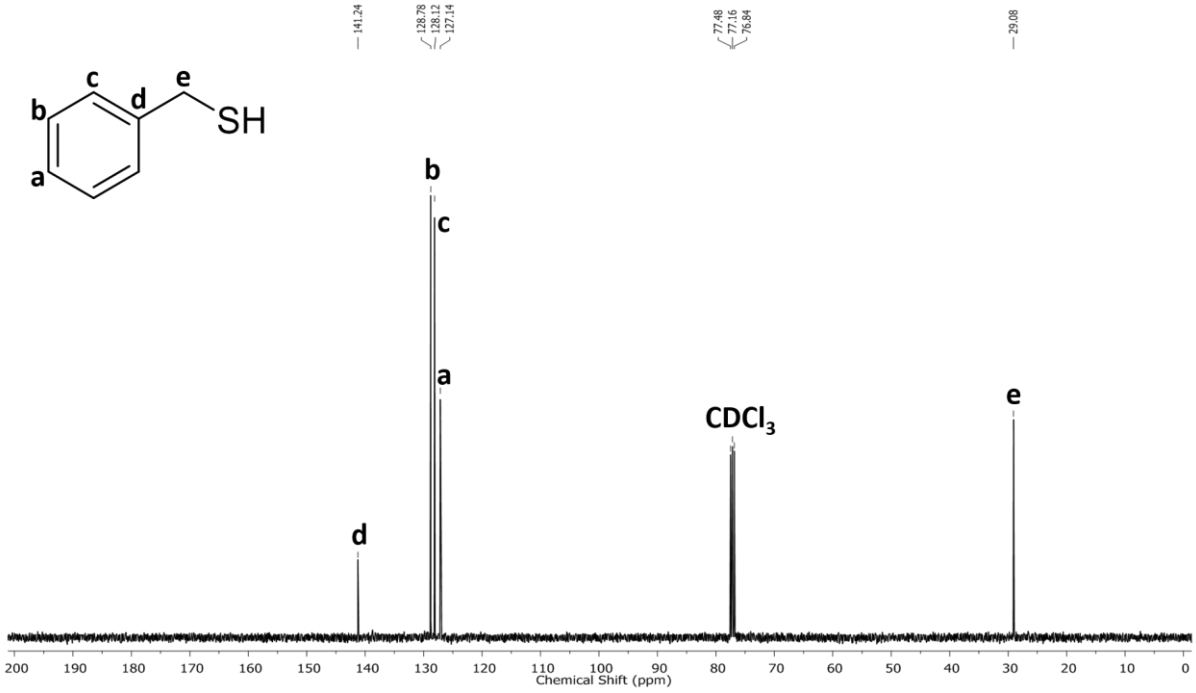


Figure S5 – ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of benzyl mercaptan.

Study of Xanthate Deprotection Kinetics by ^{1}H NMR

Benzyl Xanthate (100 mg, 0.471 mmol) along with toluene-d_8 (4.00 mL) was added to a glass vial equipped with a magnetic stirrer bar under a N_2 atmosphere. The reaction mixture (600 µL) was transferred to an NMR tube and analysed by ^{1}H NMR (400 MHz, toluene-d_8). The reaction mixture was returned to the glass vial, *n*-butyl amine (51 µL, 0.515 mmol) was added and the solution was left under magnetic stirring. After 60 seconds the reaction mixture (600 µL) was transferred to a clean NMR tube and analysed by ^{1}H NMR (400 MHz, toluene-d_8) at set time intervals over 180 minutes. The rate of deprotection was monitored by comparing the intensity of the xanthate chemical shift (4.18ppm) with respect to the solvent residual peak (2.36ppm, normalised 100H), acting as an internal standard (Figure S7, Table S1). The percent of xanthate remaining at each time point was calculated according to equation S1.

$$Xanthate\ Remaining\ (\%) = \frac{Intergral\ at\ timepoint, t}{Intergral\ at\ t = 0} \times 100$$

Equation S1 – Calculation of the percentage of xanthate remaining at time point, t, by ^{1}H NMR (400 MHz, Toluene-d_8). Calculations were made for chemical shifts at 4.18 ppm and 4.35 ppm following normalisation of the internal reference (Toluene residual solvent peak, 2.36 pm).

Table S1 – Results obtained in the study of xanthate deprotection (25 mg ml^{-1} in toluene) using ^{1}H NMR to measure the decrease in intensity of peaks at 4.18 and 4.35 ppm over 180 minutes.

Time (min)	Integral (4.18 ppm)	Integral (4.35ppm)	Xanthate Remaining (%, 4.18ppm)	Xanthate Remaining (%, 4.35ppm)
0	162.2	160.2	100.0	100.0
11	119.6	120.2	73.7	75.0
21	90.8	92.2	56.0	57.6
25	83.5	84.9	51.5	53.0
29	76.5	77.4	47.2	48.3
32	69.7	70.9	43.0	44.2
36	63.7	64.7	39.3	40.4
40	58.1	59.1	35.8	36.9
43	53.0	53.7	32.7	33.5
47	49.5	48.7	30.5	30.4
49	44.5	45.5	27.4	28.4
54	41.1	41.8	25.3	26.1
59	37.9	38.5	23.3	24.0
70	29.8	30.0	18.4	18.7
92	19.4	18.8	11.9	11.7
111	12.2	12.5	7.5	7.8
130	8.0	8.3	4.9	5.2
148	5.3	5.3	3.3	3.3
180	2.8	2.5	1.7	1.5

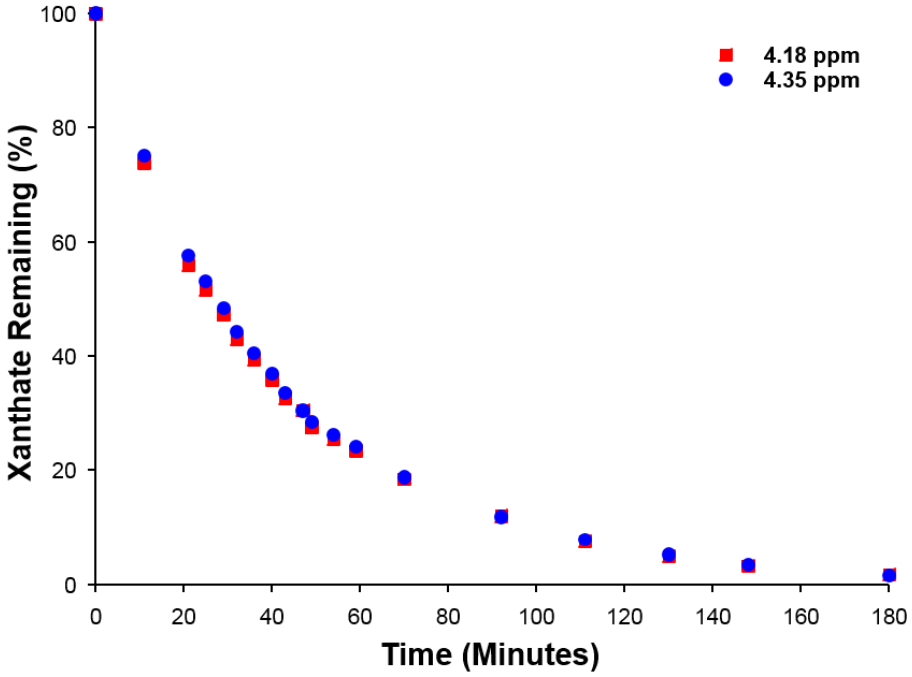


Figure S6 – Graph showing the deprotection of BzXan at (25 mg ml^{-1} in toluene) by study of the decrease in intensity of chemical shifts at 4.18 (red squares) and 4.35 ppm (blue circles) over 180 minutes.

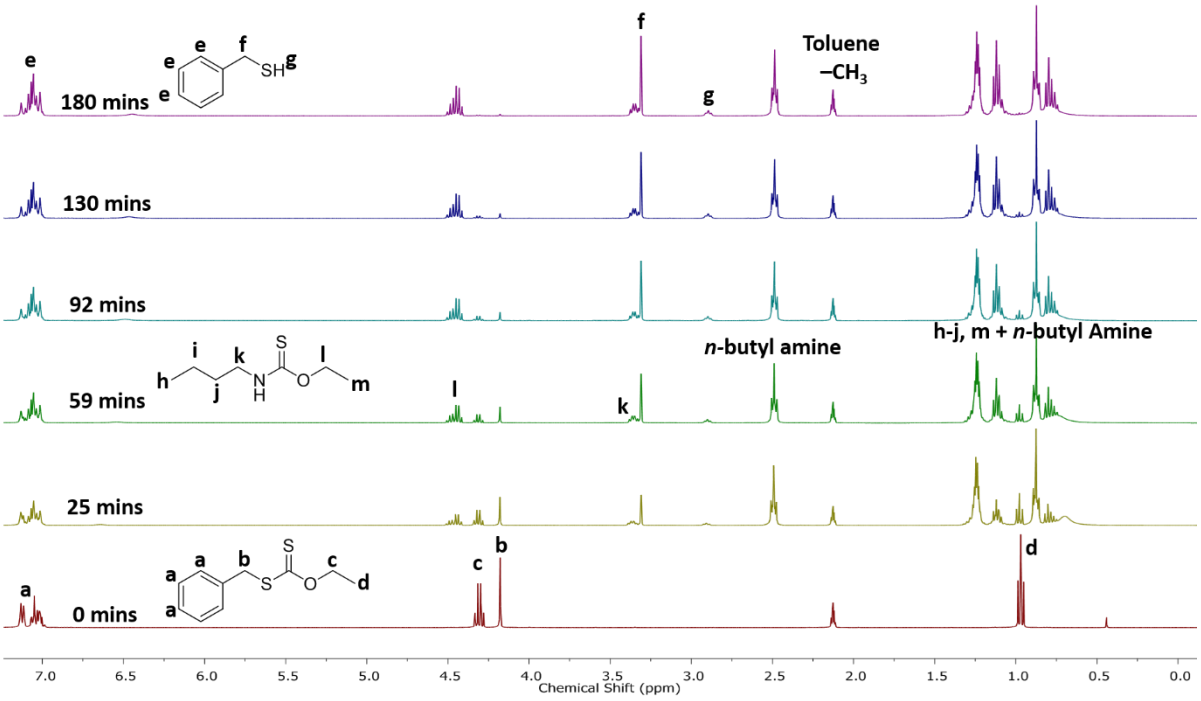


Figure S7 – Monitoring xanthate deprotection by ^{1}H NMR. Visual representation of the decrease in intensity of BzXan peaks (**b** and **c**) accompanied by the appearance of BzSH peaks (**f** and **g**) along with that of deprotection side products (**k** and **l**).

Study of Xanthate Deprotection by Ultraviolet-Visible Spectroscopy

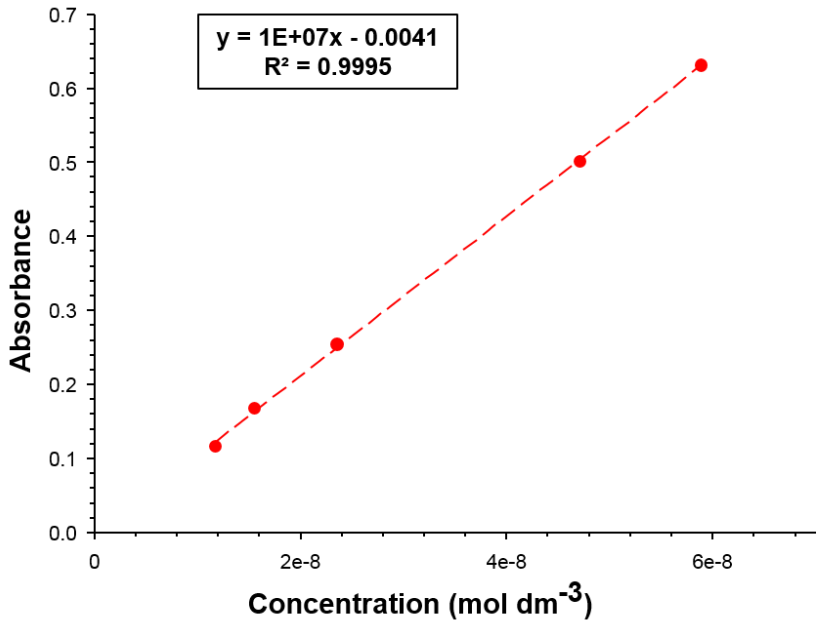


Figure S8 – Calibration curve obtained from study of the UV-Vis absorption spectra of BzXan in toluene (λ max = 287 nm).

Table S2 – Results obtained for the deprotection of BzXan at 400 mg ml^{-1} in toluene over 60 minutes by UV-Vis spectroscopy.

Time (min)	Xanthate Concentration (mol L^{-1})	Xanthate Remaining (%)	Deprotection (%)
0	8.13E-07	100.0	0
1	4.59-07	56	44
2	2.27E-07	28	72
4	1.24E-07	15	85
5	9.35E-08	12	89
6	8.28E-08	10	90
7	6.79E-08	8	92
8	5.92E-08	7	93
9	4.58E-08	6	94
10	4.26E-08	5	95
12	3.28E-08	4	96
14	2.42E-08	3	97
16	2.44E-08	3	9
18	1.75E-08	2	98
20	1.92E-08	2	98
26	1.03E-08	1	99
30	9.20E-09	1	99
35	9.07E-09	1	99
40	8.77E-09	1	99
50	8.60E-09	1	99
60	8.60E-09	1	99

Table S3 – Results obtained for the deprotection of BzXan at 25 mg ml^{-1} in toluene over 60 minutes by UV-Vis spectroscopy.

Time (min)	Xanthate Concentration (mol L^{-1})	Xanthate Remaining (%)	Deprotection (%)
0	6.46E-08	100	0
1	5.69E-08	88	12
2	5.85E-08	91	9
3	5.51E-08	85	15
4	5.29E-08	82	18
5	4.96E-08	77	23
6	4.92E-08	76	24
7	4.77E-08	74	26
8	4.30E-08	67	33
9	4.59E-08	71	29
10	4.27E-08	66	34
12	4.21E-08	65	35
14	4.00E-08	62	38
16	3.69E-08	57	43
18	3.46E-08	56	44
20	3.35E-08	52	48
25	3.17E-08	49	51
30	2.52E-08	39	61
35	2.72E-08	42	58
40	2.11E-08	33	67
45	1.93E-08	30	70
50	1.84E-08	28	72
55	1.70E-08	26	74
60	1.44E-08	22	78

Polymerisations of *n*-Butyl methacrylate

In all polymerisations, the BMA monomer was degassed by gentle bubbling of dry N_2 for 60 minutes prior to use. Polymer characterisation was conducted by ^{1}H NMR (400 MHz, $CDCl_3$) and triple detection size exclusion chromatography (TD-SEC). In all polymerisations monomer conversion was calculated by analysis of the crude reaction mixture after 16h by ^{1}H NMR.

Synthesis of Poly(*n*Butyl Methacrylate) by Conventional Free Radical Polymerisation

BMA (2.00g, 14.1 mmol), AIBN (23.2 mg, 0.141 mmol) and anhydrous toluene (2.33 mL) were added to a round bottom flask equipped with a magnetic stirrer bar. The solution was degassed for a further 15 minutes by gentle bubbling with dry N_2. The reaction flask was then sealed and placed in an oil bath, pre-heated at 80 ° C and the reaction was allowed to proceed for 16h. The reaction was stopped by removal of the flask from the oil bath thus preventing further thermal decomposition of AIBN. At this point a sample was withdrawn and diluted in $CDCl_3$ for calculation of monomer conversion by ^{1}H NMR (Figure S10, Equations S2 + S3). The crude reaction mixture was dried under reduced pressure and purified by precipitation (twice) from a minimal amount of THF into cold methanol (- 80 ° C). The purified polymer was dried *in vacuo* at 40 ° C and characterised by ^{1}H NMR and TD-SEC.

Polymerisations were also attempted in the presence of EGDMA (15 mol % w.r.t BMA) under identical conditions. In all cases a solid gel was obtained within 60 minutes of polymerisation and the reaction was aborted. Monomer conversion could not be obtained due to the insolubility of the gel.

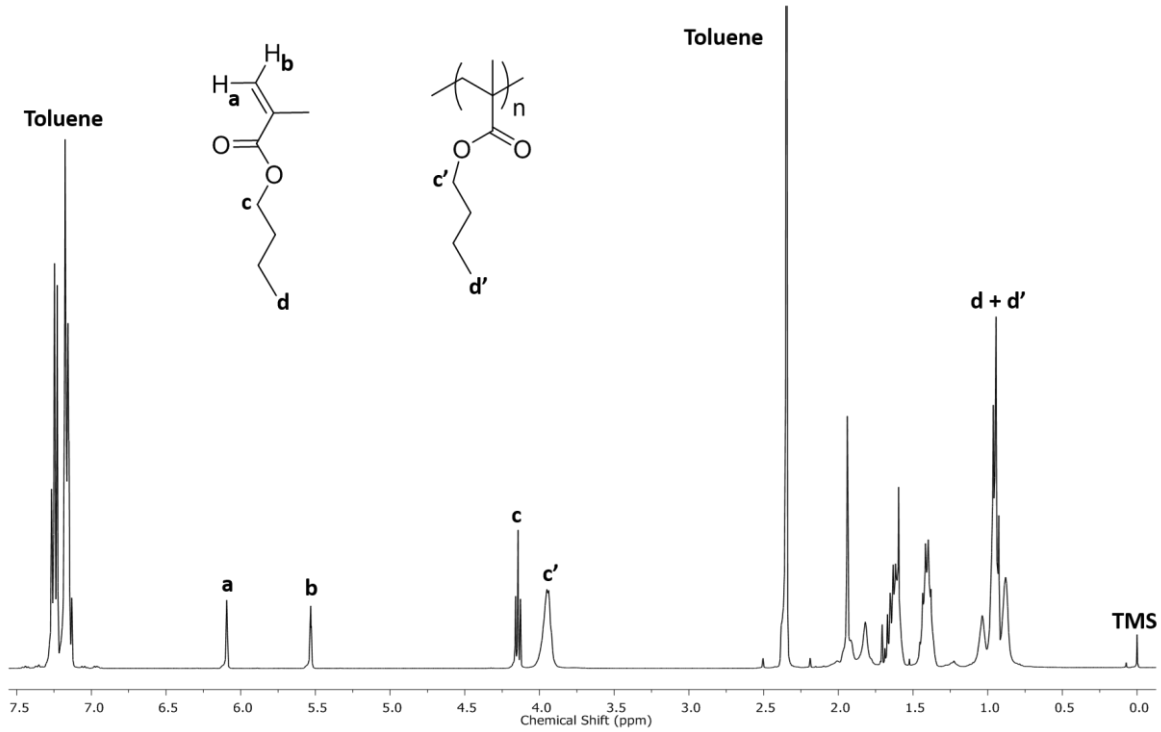


Figure S9 – ^{1}H NMR spectrum utilised for BMA conversion studies from the crude reaction mixture in $CDCl_3$.

$$\boldsymbol{Monomer\ Conversion}\ (\%) = \left(\frac{((\boldsymbol{Ic} + \boldsymbol{Ic'}) - \boldsymbol{2a})}{\boldsymbol{Ic} + \boldsymbol{Ic'}}\right) \times \boldsymbol{100}$$

Equation S2 Calculation of monomer conversion of BMA by ^{1}H NMR (400 MHz, $CDCl_3$) using the integrals obtained from the chemical shift of the OCH_2 group at ~4.0 ppm compared with remaining vinyl protons at ~6.10 ppm.

$$\boldsymbol{Monomer\ Conversion}\ (\%) = \left(\frac{((\boldsymbol{Id} + \boldsymbol{Id'}) - \boldsymbol{3Ia})}{\boldsymbol{Id} + \boldsymbol{Id'}}\right) \times \boldsymbol{100}$$

Equation S3 Calculation of monomer conversion of BMA by ^{1}H NMR (400 MHz, $CDCl_3$) using the integrals from the chemical shift of the terminal CH_3 group at ~1.0 ppm compared with remaining vinyl protons at ~6.10ppm.

Synthesis of Linear Poly(*n*Butyl Methacrylate) by CTA Mediated Free Radical Polymerisation

BMA (2.00g, 14.1 mmol), BzSH (292 mg, 2.35 mmol), AIBN (23.2 mg, 0.141 mmol) and anhydrous toluene (2.67 mL) were added to a round bottom flask equipped with a magnetic stirrer bar. The solution was degassed for a further 15 minutes by gentle bubbling with dry N_2. At this point a sample was taken (~50 µL) and diluted in $CDCl_3$ for determination of the ratio of BMA to CTA ($[M]_0$ / $[S]_0$) by ^{1}H NMR (Figure S11, calculation S4). The reaction flask was then sealed and placed in an oil bath, pre-heated at 80 °C and the reaction was allowed to proceed for 16h. The reaction was stopped by removal from the oil bath thus preventing further thermal decomposition of AIBN. At this point a sample was withdrawn and diluted in $CDCl_3$ for calculation of monomer conversion by ^{1}H NMR. The crude reaction mixture was dried under reduced pressure and purified by precipitation (twice) from a minimal amount of THF into cold methanol (- 80 ° C). The purified polymer was dried *in vacuo* at 40 °C and characterised by ^{1}H NMR (Figure S12, Equation S5) and TD-SEC.

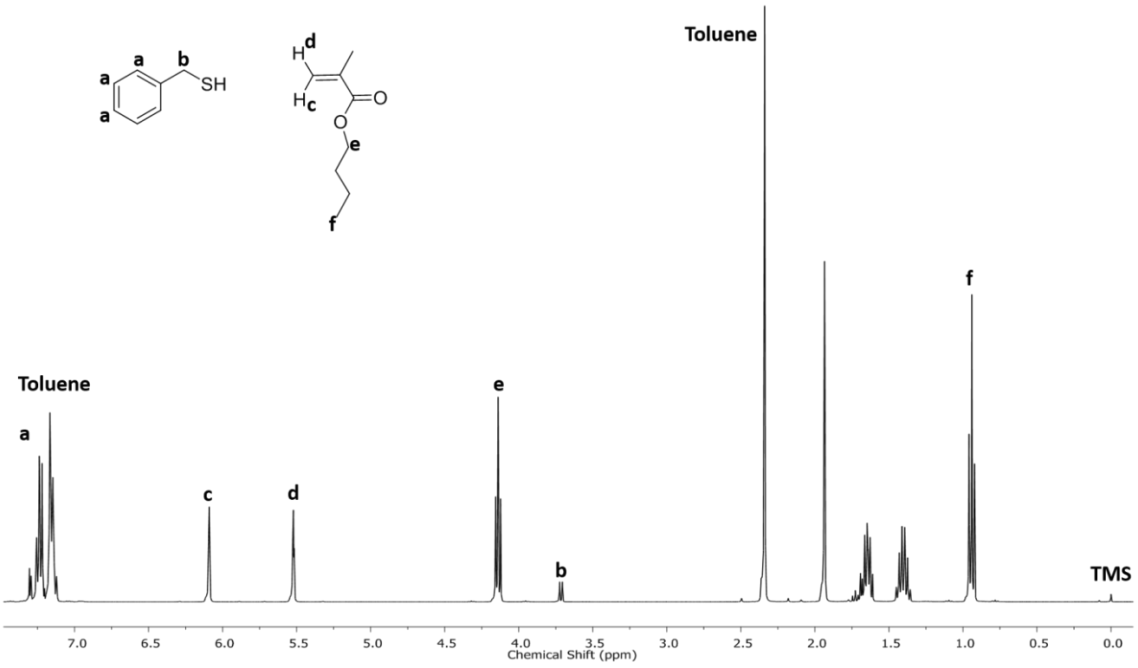


Figure S10 – ^{1}H NMR spectrum utilised for calculation of $[M]_0$ / $[S]_0$ from the crude reaction mixture in $CDCl_3$ at t_0.

$$\frac{[M]0}{[S]0} = \left(\frac{\left(\frac{Ie}{2}\right)}{\left(\frac{Ib}{2}\right)}\right)$$

Equation S4 Calculation of the ratio of monomer to CTA within the reaction mixture at t_0. Calculations are based on comparison of the integrals from chemical shifts of the CTA (b) and monomer (e).

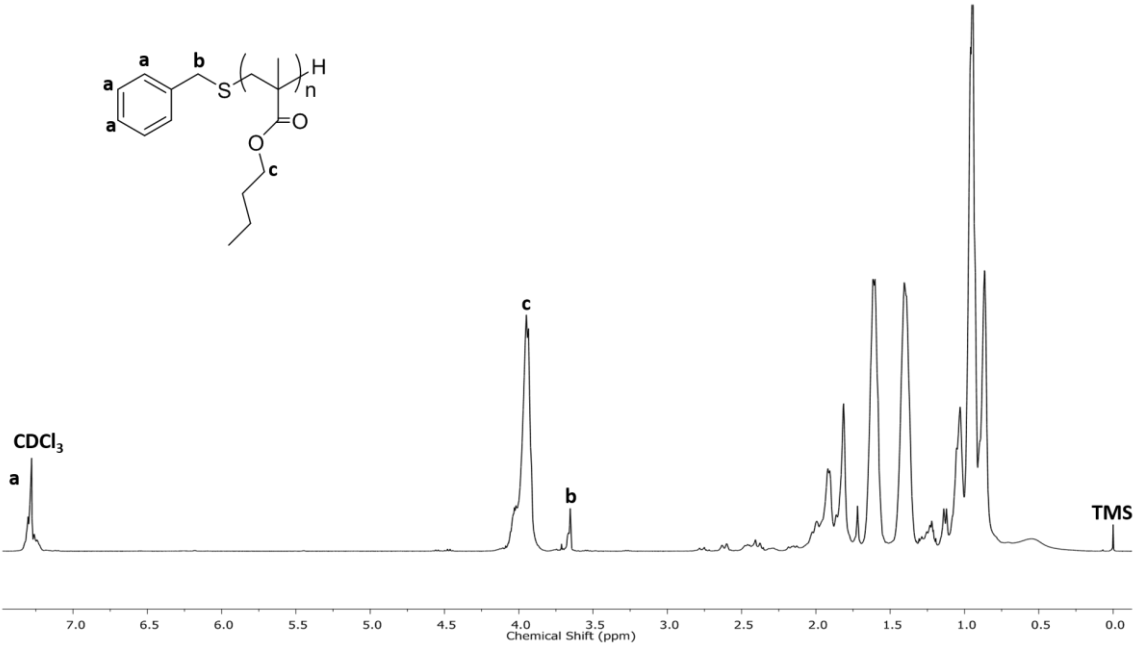


Figure S11 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) utilised for the calculation of DP_n of poly(*n*BMA) - purified polymer sample.

$$DPn = \left(\frac{\left(\frac{Ic}{2}\right)}{\left(\frac{Ib}{2}\right)}\right)$$

Equation S5 Calculation of the DP_n by ^{1}H NMR (400 MHz, $CDCl_3$) of the purified polymer. Calculations based on relative integrations of the benzyl end-group (b) and repeat unit (c).

Synthesis of Branched Poly(*n*Butyl Methacrylate) by CTA Mediated Free Radical Polymerisation

BMA (2.00g, 14.1 mmol), BzSH (292 mg, 2.35 mmol), EDGMA (419 mg, 2.12 mmol), AIBN (23.2 mg, 0.141 mmol) and anhydrous toluene (3.15 mL) were added to a round bottom flask equipped with a magnetic stirrer bar. The solution was degassed for a further 15 minutes by gentle bubbling with dry N_2. At this point a sample was taken (~50 µL) and diluted in $CDCl_3$ for determination of the ratio of BMA to CTA ($[M]_0$ / $[S]_0$) and the ratio of EGDMA to CTA ($[B]_0$ / $[S]_0$) by ^{1}H NMR (Figure S13, calculation S5). The reaction flask was then sealed and placed in an oil bath, pre-heated at 80 °C and the reaction was allowed to proceed for 16h. The reaction was stopped by removal from the oil bath thus preventing further thermal decomposition of AIBN. At this point a sample was withdrawn and diluted in $CDCl_3$ for calculation of monomer conversion by ^{1}H NMR. The crude reaction mixture was dried under reduced pressure and purified by precipitation (twice) from a minimal amount of THF into cold methanol (- 80 ° C). The purified polymer was dried *in vacuo* at 40 °C and characterised by ^{1}H NMR and TD-SEC.

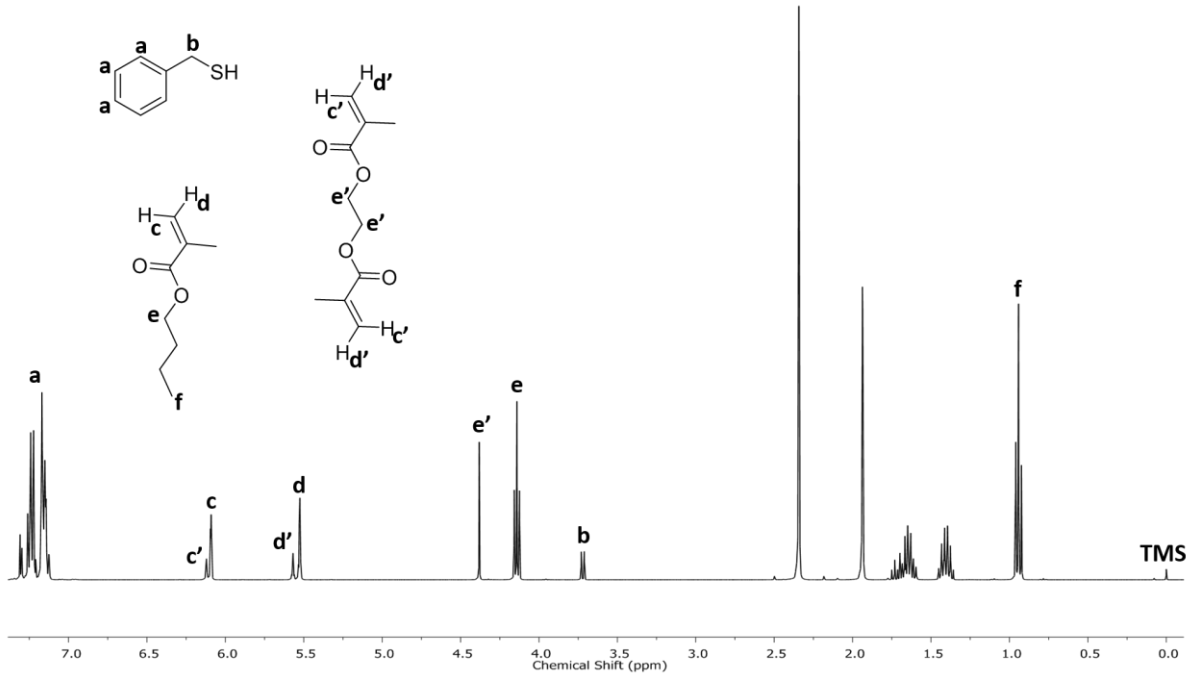


Figure S12 – ^{1}H NMR spectrum utilised for the calculation of $[B]_0$ / $[S]_0$ within the reaction mixture in $CDCl_3$ at t_0.

$$\frac{[B]0}{[S]0} = \left(\frac{\left(\frac{e'}{4}\right)}{\left(\frac{e}{2}\right)} \right)$$

Equation S6 – Calculation of $[B]_0$ / $[S]_0$ by ^{1}H NMR of the reaction mixture in $CDCl_3$ at t_0. Calculations based on relative integrations from chemical shifts of the bifunctional monomer (e') and BMA (e).

Synthesis of Linear Poly(*n*Butyl Methacrylate) by Free Radical Polymerisation Mediated by a CTA Generated by in-situ Xanthate Deprotection

BzXan (498 mg, 2.34 mmol) and anhydrous toluene (500 µL) were added to a round bottom flask purged under N_2, equipped with a magnetic stirrer bar. *n*-Butyl amine (278 µL, 2.81 mmol) was added to the flask and the reaction was allowed to proceed at ambient temperature for 2h. BMA (2.00 g, 14.1 mmol), AIBN (23.2 mg, 0.141 mmol) and anhydrous toluene (2.65 mL) were added to a glass vial and purged under gentle bubbling of dry N_2 for 30 minutes and the solution was then transferred to the round bottom flask under N_2. Once the solution was homogeneous a sample was withdrawn (~50 µL) and diluted in $CDCl_3$ for determination of $[M]_0$ / $[S]_0$ by ^{1}H NMR. The reaction flask was then sealed and placed in an oil bath, preheated at 80 °C. After 16h the reaction flask was removed from the oil bath and a sample was withdrawn (~50 µL) and diluted in $CDCl_3$ for determination of monomer conversion by ^{1}H NMR. The crude reaction mixture was dried under reduced pressure and purified by precipitation (twice) from a minimal amount of THF into cold methanol (- 80 °C). The purified polymer was dried *in vacuo* at 40 °C and characterised by ^{1}H NMR and TD-SEC.

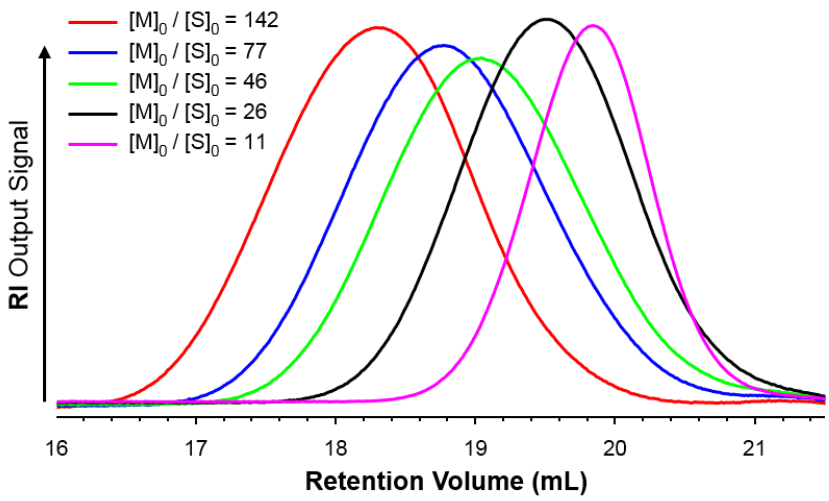


Figure S13 – Overlay of RI traces obtained by TD-SEC analysis of linear polymers synthesised using FRP mediated by a conventional CTA at varied $[M]_0$ /$[S]_0$ ratios.

Table S4 – ^{1}H NMR and TD-SEC characterisation of linear polymers synthesised using FRP mediated by a conventional CTA at varied $[M]_0$ /$[S]_0$ ratios.

Polymer	$[M]_0$ / $[S]_0$[a]	Monomer Conversion (%)[b]	M_w[c]	M_n[c]	Đ[c]	α[c]
A	142	98	24 300	16 500	1.47	0.683
B	77	97	15 500	10 100	1.53	0.64
C	46	97	11 300	6 600	1.73	0.618
D	26	97	7 100	4 300	1.65	0.568
E	11	96	3 600	2 700	1.27	0.551

Polymerisations conducted over 16h in toluene (50 wt %) using AIBN as the radical initiator (1.5 % wrt monomer) at 80 °C.[a] Obtained by 1H NMR of the reaction mixture at t_0, [b] Obtained by ^{1}H NMR of the reaction mixture at t_f, [c] Obtained by TD-SEC of the purified polymer in THF/TEA (98/2 volume %) eluent. $[M]_0$ = initial monomer concentration; $[S]_0$ = initial thiol or thiol equivalent concentration; $[B]_0$ = initial divinyl brancher concentration.

Synthesis of Branched Poly(*n*Butyl Methacrylate) by Free Radical Polymerisation Mediated by a CTA Generated by in-situ Xanthate Deprotection

BzXan (498 mg, 2.34 mmol) and anhydrous toluene (500 µL) were added to a round bottom flask purged under N_2, equipped with a magnetic stirrer bar. *n*-Butyl amine (278 µL, 2.81 mmol) was added to the flask and the reaction was allowed to proceed at ambient temperature for 2h. BMA (2.00 g, 14.1 mmol), EGDMA (419 mg, 2.12 mmol), AIBN (23.2 mg, 0.141 mmol) and anhydrous toluene (2.72 mL) were added to a glass vial and purged under a gentle bubbling of dry N_2 for 30 minutes and the solution was then transferred to the round bottom flask under N_2. Once the solution was homogeneous a sample was withdrawn (~50 µL) and diluted in $CDCl_3$ for determination of $[M]_0$ / $[S]_0$ and $[B]_0$ / $[S]_0$ by ^{1}H NMR. The reaction flask was then sealed and placed in an oil bath, preheated at 80 ° C. After 16h the reaction flask was removed from the oil bath, a sample withdrawn (~50 µL) and diluted in $CDCl_3$ for determination of monomer conversion by ^{1}H NMR. The crude reaction mixture was dried under reduced pressure and purified by precipitation (twice) from a minimal amount of THF

into cold methanol (- 80 °C). The purified polymer was dried *in vacuo* at 40 °C and characterised by ^{1}H NMR and TD-SEC.

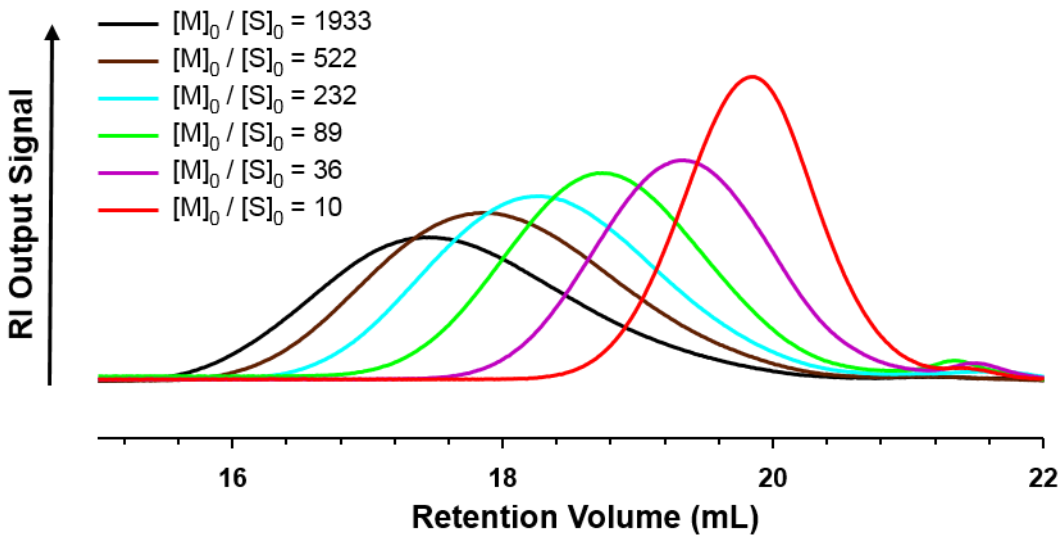


Figure S14 – Overlay of RI traces obtained by TD-SEC analysis of linear polymers synthesised using the in situ xanthate deprotection approach at varied $[M]_0$ /$[S]_0$ ratios.

Table S5 – ^{1}H NMR and TD-SEC characterisation of linear polymers synthesised using the in situ xanthate deprotection method at varied $[M]_0$ /$[S]_0$ ratios.

Polymer	$[M]_0$ / $[S]_0$[a]	Monomer Conversion (%)[b]	M_w[c]	M_n[c]	Đ[c]	α[c]
A	1933	98	55 000	29 000	1.90	0.707
B	522	98	37 000	20 400	1.82	0.695
C	232	98	25 800	15 000	1.72	0.621
D	89	98	14 200	9 000	1.58	0.658
E	36	96	8 500	5 300	1.59	0.649
F	10	96	4 300	3 400	1.29	0.496

Polymerisations conducted over 16 hours in toluene (50 wt %) using AIBN as the radical initiator (1.5 % wrt monomer) at 80 °C. [a] Obtained by 1H NMR of the reaction mixture at t_0, [b] Obtained by ^{1}H NMR of the reaction mixture at t_f, [c] Obtained by TD-SEC of the purified polymer in THF/TEA (98/2 volume %) eluent. $[M]_0$ = initial monomer concentration; $[S]_0$ = initial thiol or thiol equivalent concentration; $[B]_0$ = initial divinyl brancher concentration.

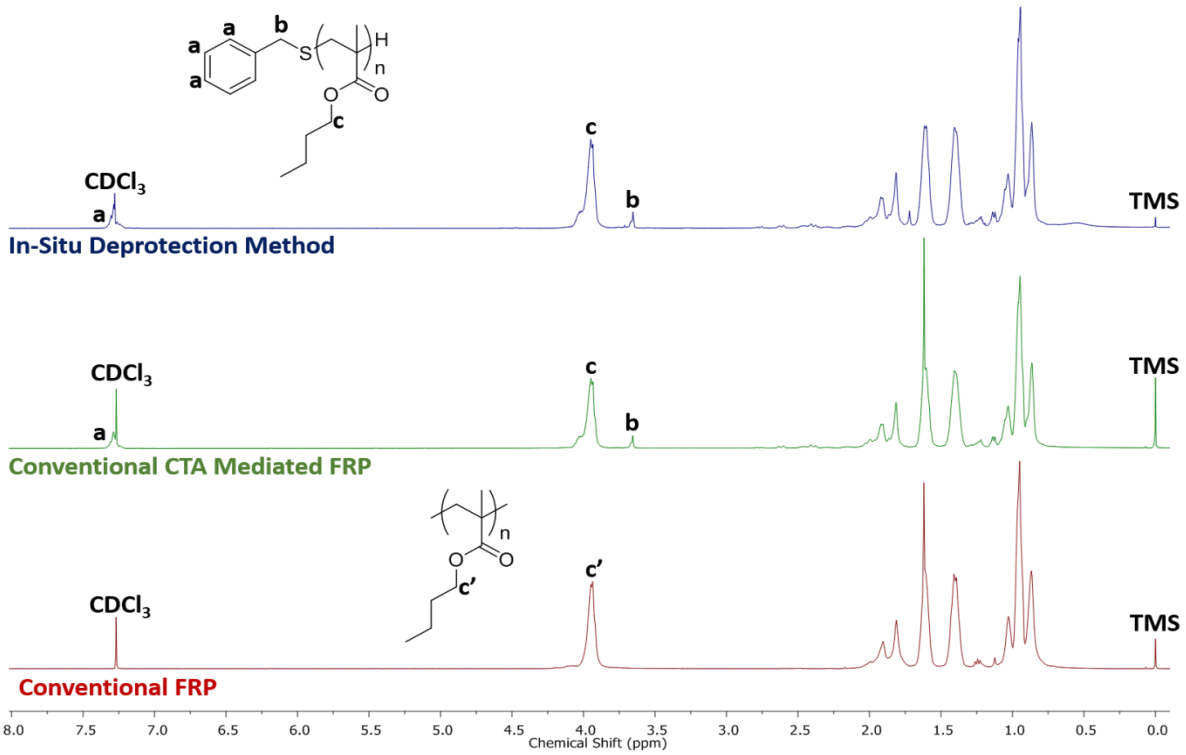


Figure S15 – Analysis of purified polymers obtained using different polymerisation approaches by ^{1}H NMR in $CDCl_3$. Qualitative evidence of chain transfer mechanism and thus incorporation of CTA functionality by appearance of aromatic (environment **a**) and thioether (environment **b**) resonances in the purified polymers. The same resonances are not observed in P(BMA) produced using conventional FRP.

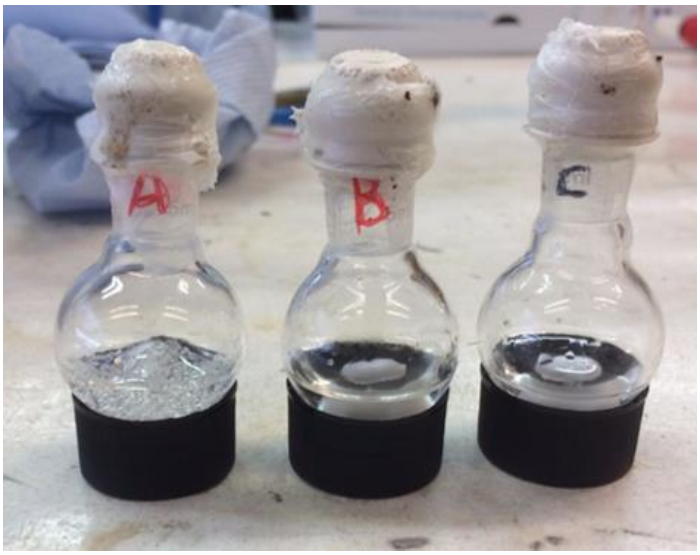


Figure S16 – Visual representation of the crude reaction mixture for the (attempted) branching polymerisations of BMA with EGDMA at varied $[B]_0$ / $[S]_0$ ratios, using the in situ xanthate deprotection method. (A) An insoluble gel network was obtained for $[B]_0$ / $[S]_0$ = 0.93. (B + C) Soluble branched polymers were obtained for branching polymerisations conducted at $[B]_0$ / $[S]_0$ = 0.88 and 0.76 for B and C respectively.

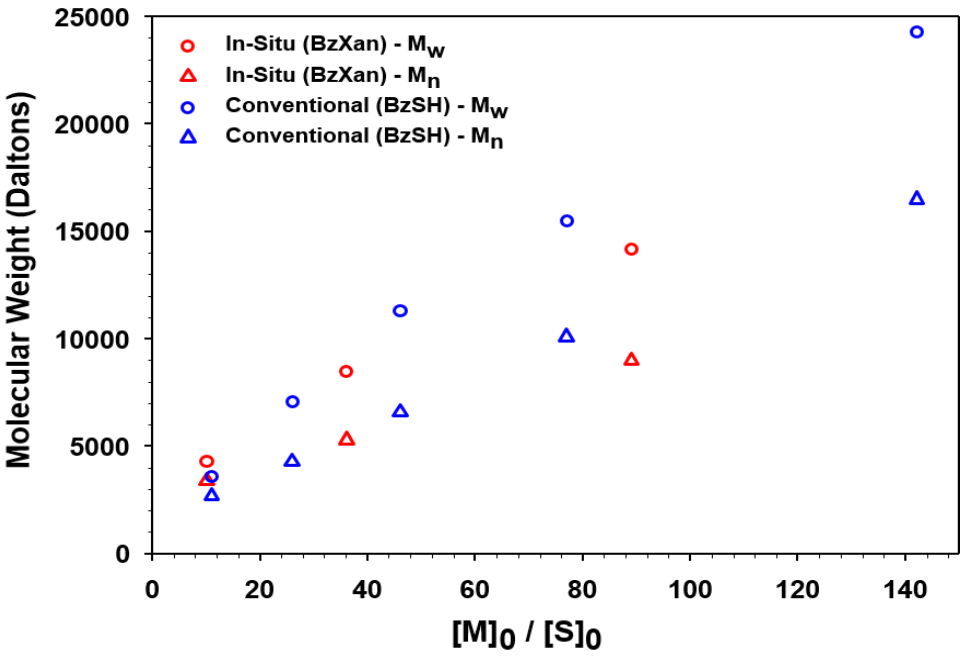


Figure S17 – Comparison of molecular weight data (M_w and M_n) obtained by SEC for linear polymerisations conducted using conventional CTA and in-situ deprotection methods across varied $[M]_0/[S]_0$ ratios. Data obtained from Table S4 & S5.