Electronic Supplementary Material (ESI) for Chemical Science.

SUPPORTING INFORMATION

FOR

Fluorescent and chemico-fluorescent responsive polymers from dithiomaleimide and dibromomaleimide functional monomers

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EXPERIMENTAL

Materials and apparatus

Tert-butyl acrylate (tBA) was vacuum distilled over CaH_2 prior to use, and stored at 4 °C. Methyl methacrylate (MMA) was passed through a column of neutral alumina (Al_2O_3) prior to use, and stored at 4 °C. 2,2'-azobis(2-methylpropionitrile) (AIBN) was recrystallized twice from methanol and stored at 4 °C in the dark. The RAFT agents 2-cyano-2-propyl benzodithioate (CPBD) and cyanomethyl dodecyl trithiocarbonate (CMDT) were purchased from Aldrich and used as received. All other chemicals and reagents were purchased from Aldrich and used as received. Solvents were purchased from Fisher Scientific and used as received.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX-300, DPX-400 or DRX-500 spectrometer in $CDCl_3$ unless otherwise stated. Chemical shifts are given in ppm downfield from the internal standard tetramethylsilane. Size exclusion chromatography (SEC) measurements were conducted using a Varian 390-LC-Multi detector suite fitted with differential refractive index (DRI), and UV/Vis or and photodiode array (PDA) detectors. A guard column (Varian Polymer Laboratories PLGel 5 µm, 50 × 7.5 mm) and two mixed D columns (Varian Polymer Laboratories PLGel 5 µm, 300 × 7.5 mm) were used. The mobile phase was tetrahydrofuran with 2 % triethylamine, or chloroform with 2 % triethylamine eluent at a flow rate of 1.0 ml/min. Data was analysed using Cirrus v3.3 with calibration curves produced using Varian Polymer laboratories Easi-Vials linear poly(styrene) standards (162 Da – 240 kDa). Infrared spectra were recorded (neat) on a Perkin Elmer, Spectrum 100 FT-IR Spectrometer. High Resolution Mass Spectrometry (HR-MS) were conducted on a Bruker UHR-Q-ToF MaXis with electrospray ionization. Fluorescence spectra were collected on a PerkinElmer LS 55 Fluorescence Spectrometer. UV/Vis spectra and temperature dependant light transmission were recorded on a PerkinElmer LAMBDA 35 UV/Vis Spectrophotometer. High pressure liquid chromatograms were recorded on a Varian 9250 HPLC, fitted with a Supelco Discovery C18 column and a PDA and fluorescence detector. The mobile phase was a gradient of water and methanol.

Synthetic protocols

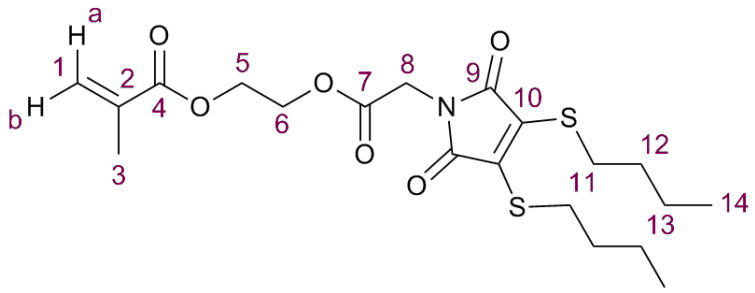
2-[(2-bromoacetyl)oxy]ethyl 2-methylprop-2-enoate (bromoacetyl methacrylate) was synthesised in a single step as previously reported.[1]

2-[(2-bromoacetyl)oxy]ethyl prop-2-enoate (bromoacetyl acrylate) was synthesised in a single step as previously reported.[2]

3,4-bis(butylsulfanyl)-2,5-dihydro-1H-pyrrole-2,5-dione (**1**) was synthesised as previously reported.[3]

Triethylene glycol monomethylether methacrylate (TEGA) was synthesised as previously reported.[4]

2-([2-(3,4-bis[butylsulfanyl]-2,5-dioxo-2,5-dihydro-1H-pyrrol-1-yl)acetyl]oxy)ethyl 2-methylprop-2-enoate (DTMMA)



To a suspension of K_2CO_3 (1.12 g, 8.08 mmol) and tetrabutylammonium iodide (0.199g 0.539 mmol) in acetone was added solutions of 1 (1.62 g, 5.93 mmol) and bromoacetyl methacrylate (1.35 g, 5.39 mmol) in acetone to a final volume of 250 ml. The solution was stirred at room temperature for 50 h, before the solution was filtered and the solvent removed *in vacuo*. The crude product was purified by column chromatography (SiO_2, petroleum ether : dichloromethane = 3:7) to yield the product as an off-yellow oil (1.6 g, 67%). R_f = 0.16. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.14 (1H, m, H1a), 5.61 (1H, quin, J = 1.5 Hz, H1b), 4.41 (2H, m, H6) 4.35 (2H, m, H5), 4.28 (2H, s), 3.30 (4H, t, J = 7.5 Hz, H11), 1.95 (3H, t, J = 1.5 Hz, H3), 1.64 (4H, m, H12), 1.44 (4H, sex, J = 7.5 Hz, H13), 0.93 (6H, t, J = 7.5 Hz, H14); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.1 (C7) 167.0 (C4), 165.7 (C9), 136.2 (C10) 135.8 (C2), 126.4 (C1), 63.4 (C6), 62.0 (C5), 39.1 (C8), 32.5 (C12), 31.6 (C11), 21.7 (C13), 18.3 (C3), 13.6 (C14) ; FTIR (neat) ν_{max} / cm^{-1} 1755 (C=O stretch ester), 1706 (C=O stretch maleimide), 1638 (C=C stretch methacrylate); HR-MS (MaXis) m/z found 466.1322, calc. 466.1329 ($[M+Na]^+$, 100 %).

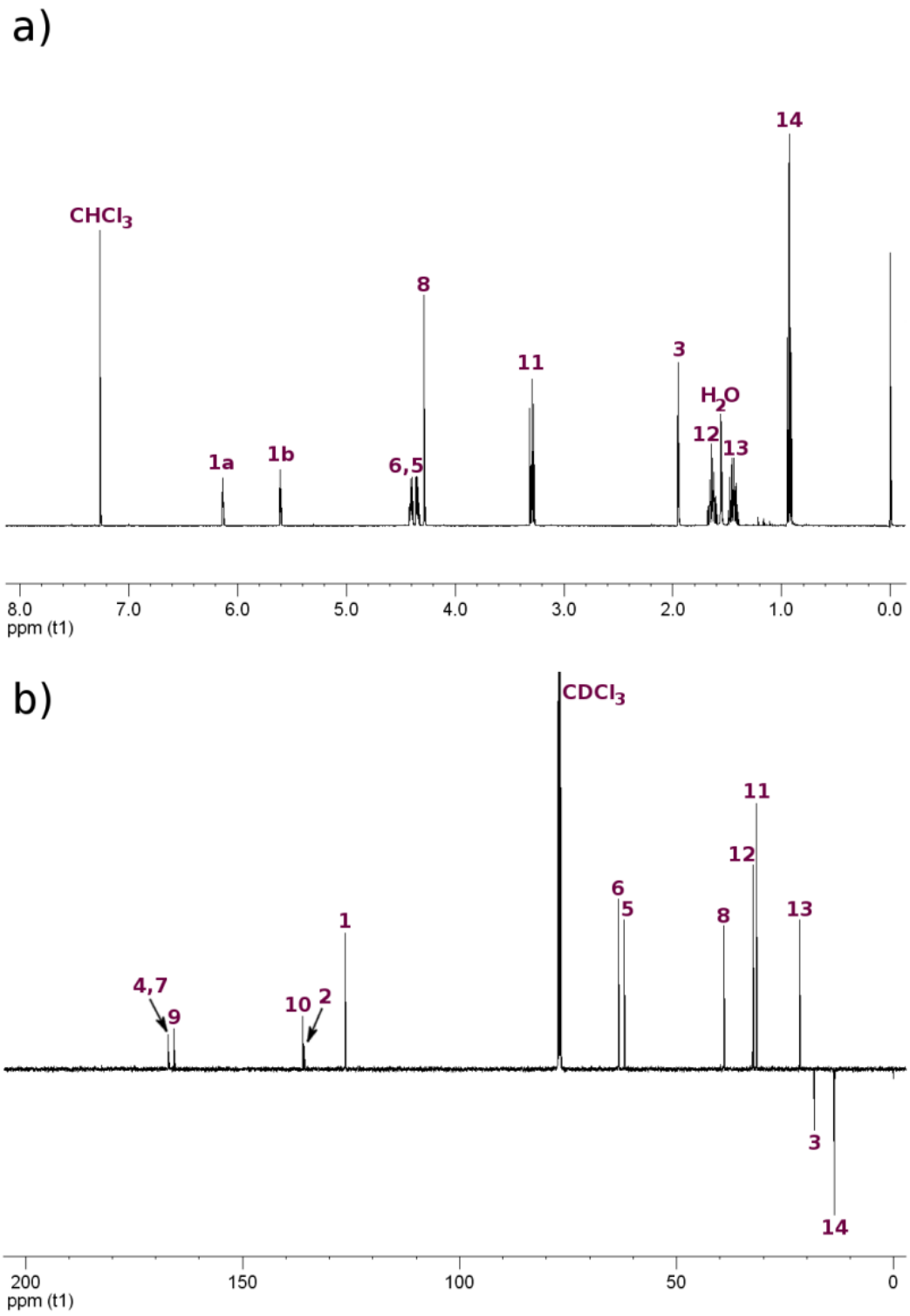
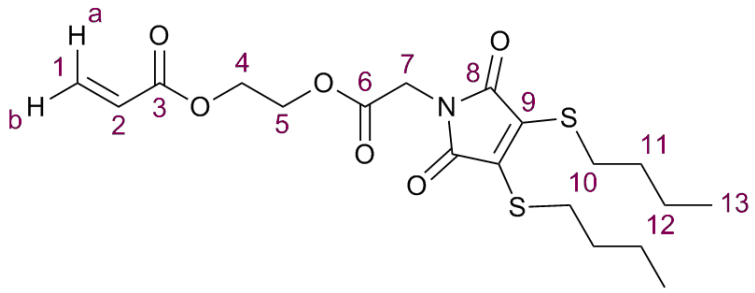


Figure S1. a) ^{1}H NMR (400 MHz, $CDCl_3$) spectrum and b) ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **DTMMA**.

2-[(2-[3,4-bis(butylsulfanyl)-2,5-dioxo-2,5-dihydro-1H-pyrrol-1-yl]acetyl)oxy]ethyl prop-2-enoate (DTMA)



To a suspension of K_2CO_3 (1.44 g, 10.4 mmol) in acetone (200 ml) was added bromoacetyl acrylate (1.65 g, 6.97 mmol), and **1** (2g, 7.32 mmol). The solution was stirred at room temperature for 44 h, it was filtered, and the solvent removed from the filtrate *in vacuo*. The crude product was then purified by column chromatography (SiO_2, petroleum ether : dichloromethane gradient 2:1–1:2) to yield the product as a yellow oil (2.27 g, 76%). R_f = 0.21 (petroleum ether: dichloromethane = 1:2). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.45 (1H, dd, J = 17.5 Hz, J = 1.5 Hz, H1a), 6.15 (1H, dd, J = 17.5 Hz, J = 10.5 Hz, H2), 5.89 (1H, dd, J = 10.5 Hz, J = 1.5 Hz, H1b), 4.38 (4H, m, H4 & H5), 4.29 (2H, s, H7), 3.30 (4H, t, J = 7.5 Hz, H10), 1.64 (4H, quin, J = 7.5 Hz, H11), 1.45 (4H, sex, J = 8.0 Hz, H12), 0.93 (6H, t, J = 7.5 Hz, H13); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.5 (C6), 165.2 (C8), 165.1 (C3), 135.5 (C9), 131.0 (C1), 127.2 (C2), 62.8 (H5), 61.2 (H4), 38.5 (C7), 31.8 (C11), 31.0 (C10), 21.0 (C12), 13.0 (C13); FTIR (neat) ν_{max} / cm^{-1}, 1755 (C=O stretch ester), 1727 (C=O stretch acrylate), 1706 (C=O stretch maleimide), 1637 (C=C stretch acrylate), 1620 (C=C stretch maleimide); HR-MS (MaXis) m/z found 452.1179, calc. 452.1172 ([M+Na]$^+$, 100 %).

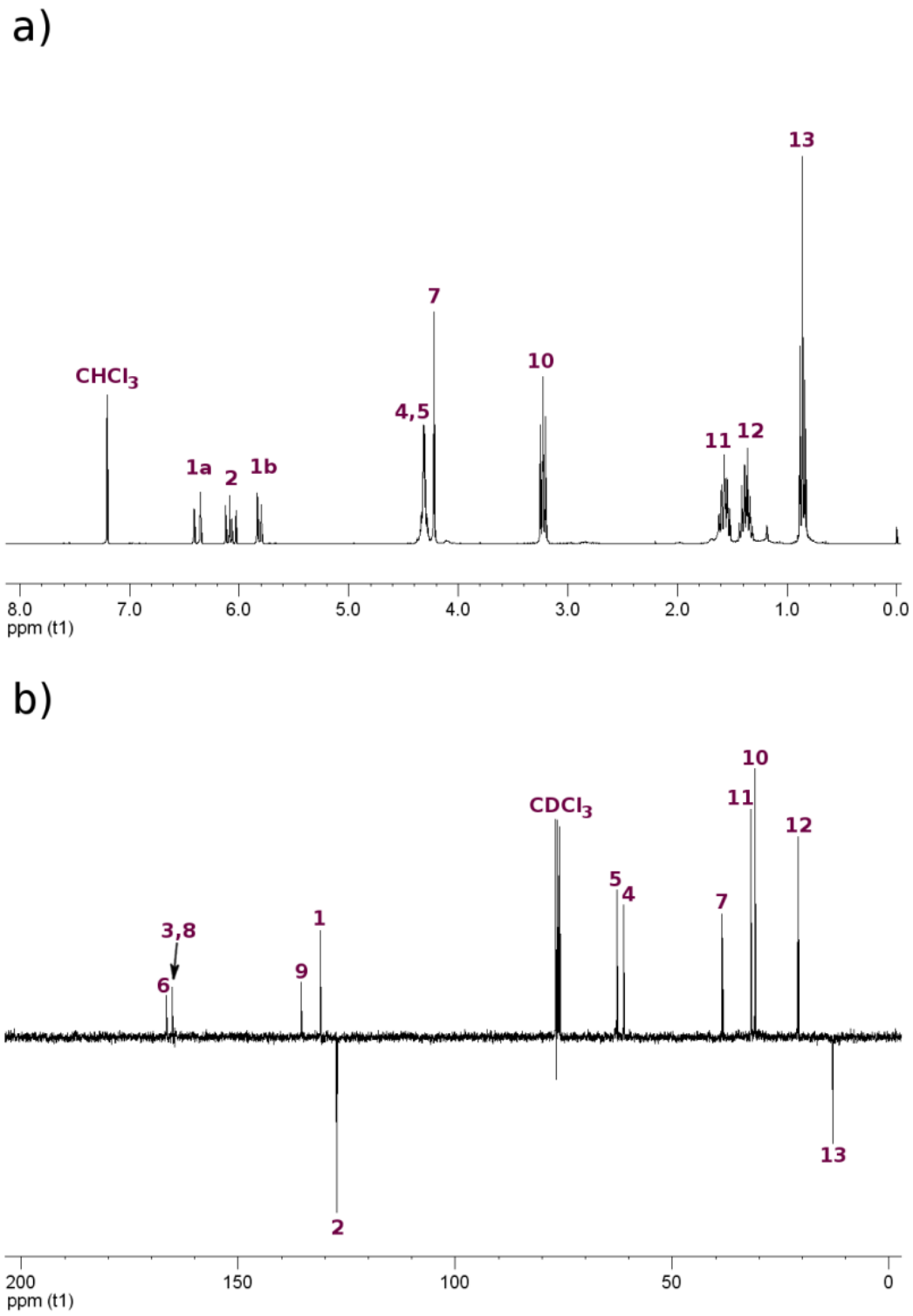
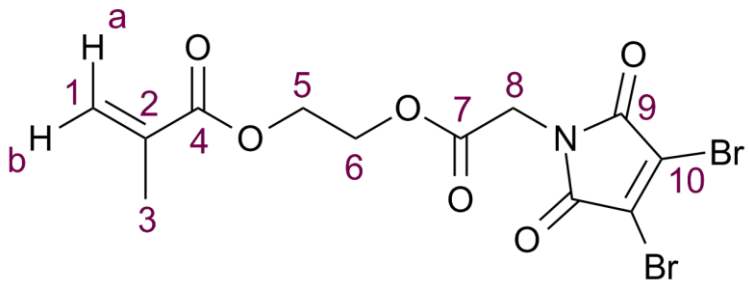


Figure S2. a) ^{1}H NMR (300 MHz, $CDCl_3$) spectrum and b) ^{13}C NMR (75 MHz, $CDCl_3$) spectrum for **DTMA**.

2-[(2-[3,4-dibromo-2,5-dioxo-2,5-dihydro-1H-pyrrol-1-yl]acetyl)oxy]ethyl 2-methylprop-2-enoate (DBMMA)



To a solution of 2,3-Dibromomaleimide (3.91 g, 15.3 mmol), K_2CO_3 (2.12 g, 15.3 mmol) and tetrabutylammonium iodide (0.513 g, 1.39 mmol) in acetone (200 ml) was added dropwise bromoacetyl methacrylate (3.50 g, 13.9 mmol). The solution was stirred at room temperature for 16 h, before the solvent was removed *in vacuo*. Water (200 ml) was added, and the crude product extracted with diethyl ether (200 ml x 3). The combined organic layers were washed with brine (200 ml x 2), and dried with $MgSO_4$. The solvent was removed from the organic layer *in vacuo* and the crude product was purified by column chromatography (SiO_2, petroleum ether : diethyl ether = 3:1) to yield the product as an off-white solid (2.27 g, 76%). R_f = 0.23. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.13 (1H, quin, J = 1.5 Hz, H1a), 5.62 (1H, quin, J = 1.5 Hz, H1b), 4.43 (2H, m, H6), 4.39 (2H, s, H8), 4.36 (2H, m, H5), 1.95 (3H, t, J = 1.6 Hz, H3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0 (C4), 166.4 (C9), 163.1 (C7), 135.7 (C2), 129.9 (C10), 126.4 (C1), 63.8 (C6), 61.9 (C5), 40.0 (C8), 18.3 (C3); FTIR (neat) ν_{max} / cm^{-1} 1793 (C=O stretch maleimide), 1749 (C=O stretch ester), 1717 (C=O stretch acrylate), 1706 (C=O stretch maleimide), 1632 (C=C stretch acrylate), 1593 (C=C stretch maleimide); HR-MS (MaXis) m/z found 423.9027, calc. 423.9026 ($[M+H]^+$, 100 %).

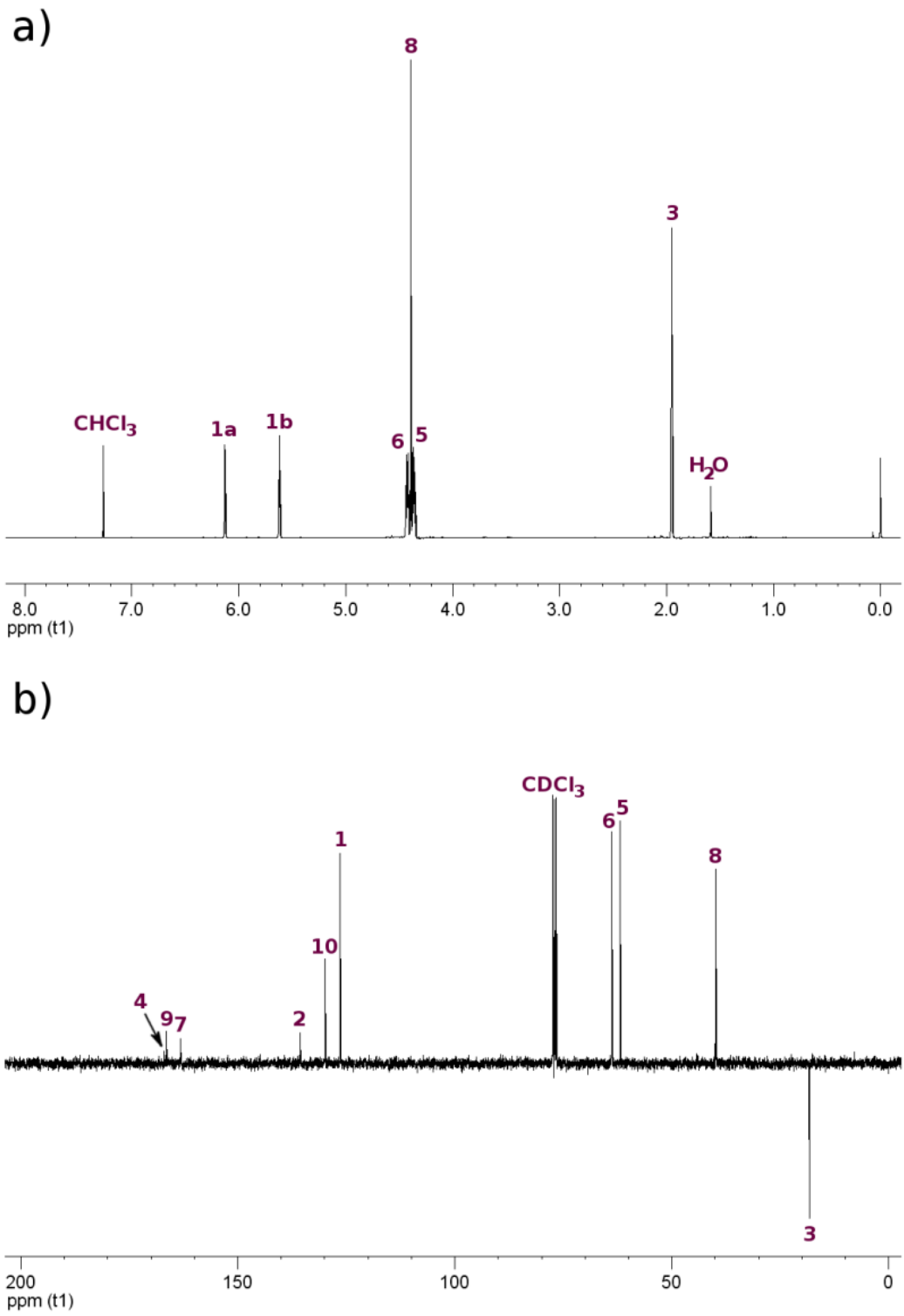
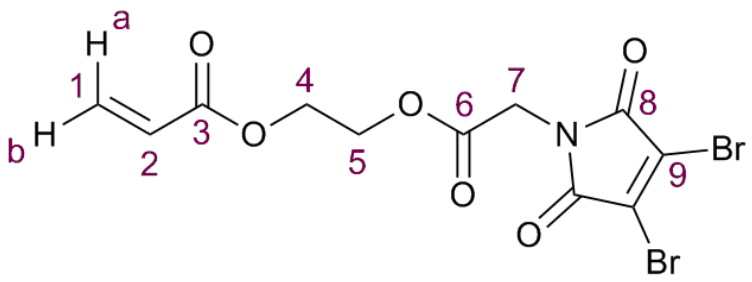


Figure S3. a) ^{1}H NMR (400 MHz, $CDCl_3$) spectrum and b) ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **DBMMA**.

2-[(2-[3,4-dibromo-2,5-dioxo-2,5-dihydro-1H-pyrrol-1-yl]acetyl)oxy]ethyl prop-2-enoate (DBMA)



To a solution of 2,3-Dibromomaleimide (5.39 g, 21.1 mmol) and K_2CO_3 (2.92 g, 21.1 mmol) in acetone (200 ml) was added dropwise bromoacetyl acrylate (4.56 g, 19.2 mmol). The solution was stirred at room temperature for 16 h, before the solvent was removed *in vacuo*. The residue was dissolved in diethyl ether (300 ml) and washed with water (200 ml x 6), brine (200 ml), and dried with $MgSO_4$. The solvent was removed from the organic layer *in vacuo* and the crude product was purified by column chromatography (SiO_2, petroleum ether : diethyl ether = 3:1) to yield the product as an off-white powder (5.01 g, 68%). R_f = 0.14. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.45 (1H, dd, J = 17.5 Hz, J = 1.5 Hz, H1a), 6.14 (1H, dd, J = 17.5 Hz, J = 10.5 Hz, H2), 5.89 (1H, dd, J = 10.5 Hz, J = 1.5 Hz, H1b), 4.42 (2H, m, H5), 4.40 (2H, s, H7), 4.38 (2H, m, H4); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4 (C3), 165.8 (C8), 163.1 (C6), 131.8 (C1), 129.9 (C9), 127.8 (C2), 63.8 (C5), 61.7 (C4), 40.0 (C7); FTIR (neat) ν_{max} / cm^{-1} 1792 (C=O stretch maleimide), 1748 (C=O stretch ester), 1724 (C=O stretch acrylate), 1711 (C=O stretch maleimide), 1630 (C=C stretch acrylate), 1589 (C=C stretch maleimide); HR-MS (MaXis) m/z found 409.8870, calc. 409.8869 ($[M+H]^+$, 100 %).

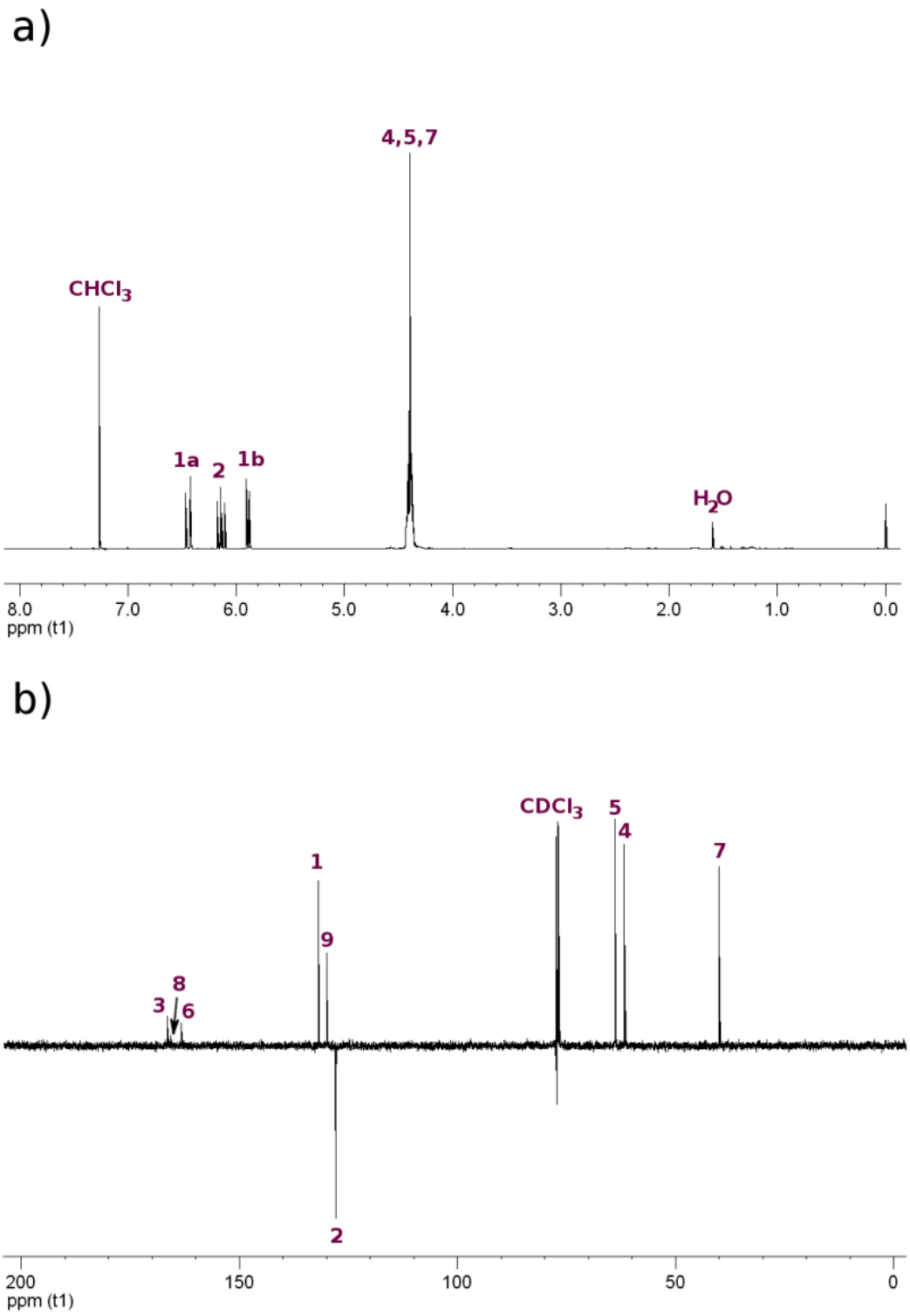


Figure S4. a) ^{1}H NMR (400 MHz, $CDCl_3$) spectrum and b) ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **DBMA**

General procedure for RAFT copolymerisations

Typically; to a polymerisation ampoule was added a solution of RAFT agent, AIBN, and monomers in dioxane. The solution was degassed by three freeze-pump-thaw cycles, the ampoule sealed under N_2 and the reaction stirred at 65 °C. Periodically samples were taken for ^{1}H NMR spectroscopy and SEC analysis.

	CTA (mg, µmol)	Monomers (g, mmol)		AIBN (mg, µmol)	Dioxane (ml)
P1	CPBD (20.0, 90.4)	MMA (0.407, 4.07)	DTMMA (0.200, 0.452)	(1.48, 9.04)	(0.483)
P2	CPBD (10.0, 45.2)	OEGMA (0.592, 2.03)	DTMMA (0.100, 0.226)	(0.742, 4.52)	(1.25)
P3	CMDT (20.0, 63.0)	^{t}BA (0.363, 2.83)	DTMA (0.135, 0.315)	(1.03, 6.30)	(0.457)
P4	CMDT (10.0, 31.5)	TEGA (0.309, 1.42)	DTMA (0.068, 0.157)	(0.517, 3.15)	(0.616)
P5	CPBD (20.0, 90.4)	MMA (0.407, 4.07)	DBMMA (0.192, 0.452)	(1.48, 9.04)	(0.483)
P6	CPBD (10.0, 45.2)	OEGMA (0.592, 2.03)	DBMMA (0.096, 0.226)	(0.742, 4.52)	(1.25)
P7	CMDT (26.3, 82.7)	^{t}BA (0.477, 3.72)	DBMA (0.170, 0.413)	(1.36, 8.27)	(0.600)
P8	CMDT (10.0, 31.5)	TEGA (0.309, 1.42)	DBMA (0.065, 0.157)	(0.517, 3.15)	(0.616)
P9	CPBD (10.0, 45.2)	OEGMA (0.657, 2.26)	-	(0.742, 4.52)	(1.25)
P10	CMDT (10.0, 31.5)	TEGA (0.344, 1.57)	-	(0.517, 3.15)	(0.616)
P11	CPBD (20.0, 90.4)	OEGMA (1.18, 4.07)	DBMMA (0.192, 0.452)	(1.48, 9.04)	(1.48)

P(MMA-*co*-DTMMA) (**P1**) and P(MMA-*co*-DBMMA) (**P5**) were isolated by repeated precipitation from THF into ice-cold methanol.

P(OEGMA-*co*-DTMMA) (**P2**), P(TEGA-*co*-DTMA) (**P4**), and P(OEGMA-*co*-DBMMA) (**P6** and **P11**)were isolated by repeated precipitation from dioxane into ice-cold hexanes, followed by exhaustive dialysis against deionized water (MWCO = 3.5 kDa) and lyophilisation.

P(tBA-*co*-DTMA) (**P3**) and P(tBA-*co*-DBMA) (**P7**) were isolated by repeated precipitation from DCM into cold (-78 °C) methanol/water (9/1 v/v).

P(TEGA-*co*-DBMA) (**P8**), P(OEGMA) (**P9**), and P(TEGA) (**P10**) were isolated by exhaustive dialysis against deionized water (MWCO = 3.5 kDa) and lyophilisation.

General procedure for the post-polymerisation functionalisation of P(OEGMA$_{27.6}$-*co*-DBMMA$_{4.7}$) (P11) with thiols (P12-15)

Typically; **P11** (40 mg, 3.9 µmol) was dissolved in pH 6 buffer (4 ml, 100 mM sodium phosphate, 150 mM NaCl). To this solution was added a solution of thiol in DMF (46.8 µl of a 1 M solution) upon which the solution immediately turned yellow/green in colour. The reaction was stirred at room temperature for 30 mins, before addition of an excess of deionised water, and dialysis against deionised water (MWCO 3.5 kDa). The product was isolated by lyophilisation.

Post-polymerisation functionalisation of P(OEGMA$_{27.6}$-*co*-DBMMA$_{4.7}$) (P11) with 3-mercaptopropionic acid, monitored by UV-vis spectroscopy

P11 (1.5 mg, 0.146 µmol) was dissolved in pH 6 buffer (1.5 ml, 100 mM sodium phosphate, 150 mM NaCl) and added to a quartz cuvette, and a full UV-vis spectrum was recorded. Then, a solution of 3-mercaptopropionic acid in DMF (1.76 µl of a 1 M solution) was added to the cuvette, and the absorption at 409 nm measured for 3 h.

Thiol-exchange reaction of P(TEGA$_{31.6}$-*co*-DTMA$_{3.4}$) (P4) with thiophenol (P16)

P4 (40 mg, 4.9 µmol) containing an average of 3.4 DTM units per chain (16.7 µmol) was dissolved in pH 6 buffer (4 ml, 100 mM sodium phosphate, 150 mM NaCl). To this solution was added a solution of thiophenol in DMF (112 µl of a 2.5 M solution). The reaction was stirred at room temperature for 2 h, before addition of an excess of deionised water, and dialysis against deionised water (MWCO 3.5 kDa). The product was isolated by lyophilisation.

Emission spectra of the reaction mixture were recorded at a 10× dilution, with λ_{ex} = 435 nm.

SUPPLEMENTARY FIGURES

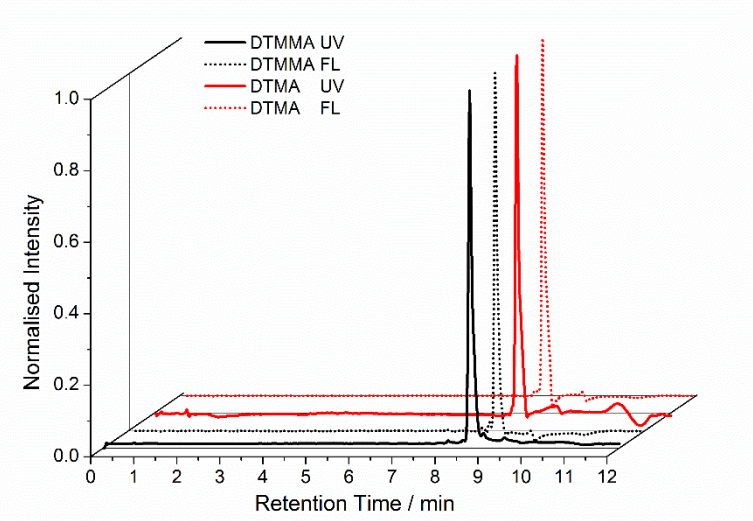


Figure S5. HPLC spectra for the fluorescent monomers DTMMA and DTMA, with UV (solid lines, λ_{abs} = 260 nm) and fluorescence (dotted lines, λ_{ex} = 420 nm, λ_{em} = 520 nm) detection.

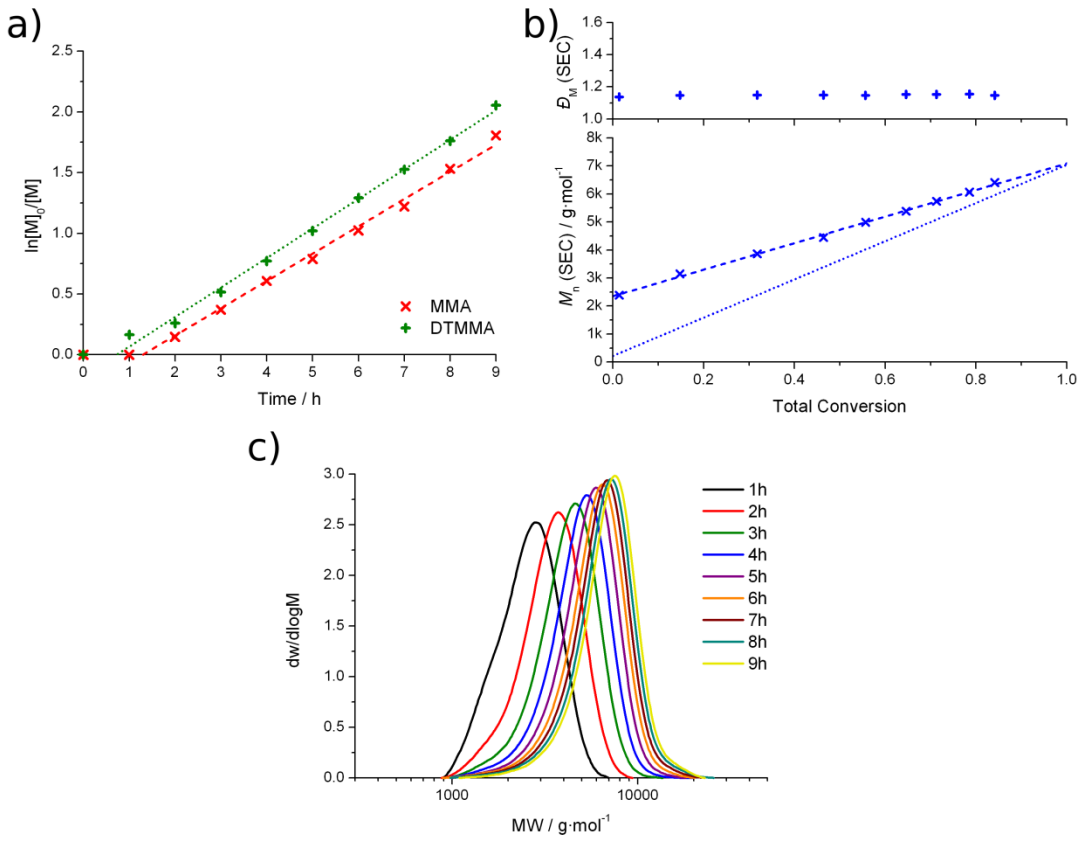


Figure S6. DTMMA/MMA copolymerisation **P1**; a) First order kinetics of DTMMA and MMA consumption with linear fits; b) M_n and $Đ_M$ (as measured by SEC) as a function of total monomer conversion with linear fit (dashed line - - -) and theoretical values (assuming equivalent rates of conversion for both monomers, dotted line · · ·); c) Evolution of molecular weight distribution (as measured by SEC) as a function of time.

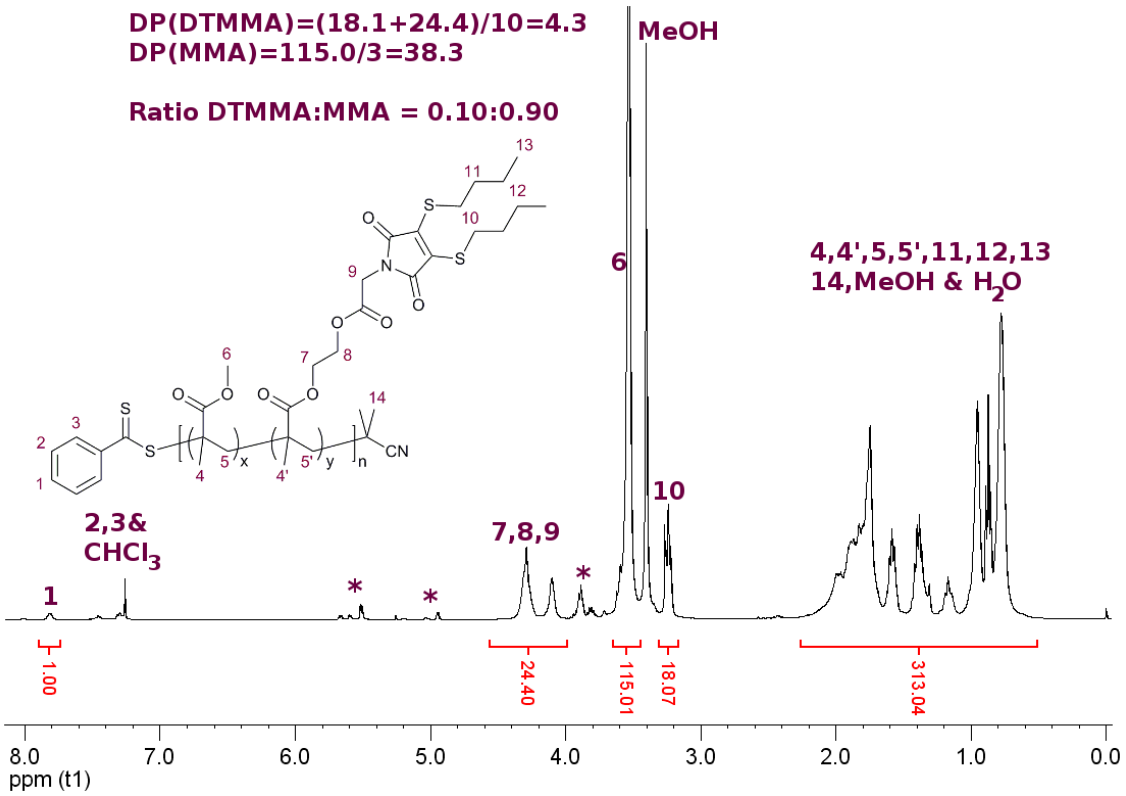


Figure S7. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **P1**. Peaks marked with * correspond to THF peroxide impurities

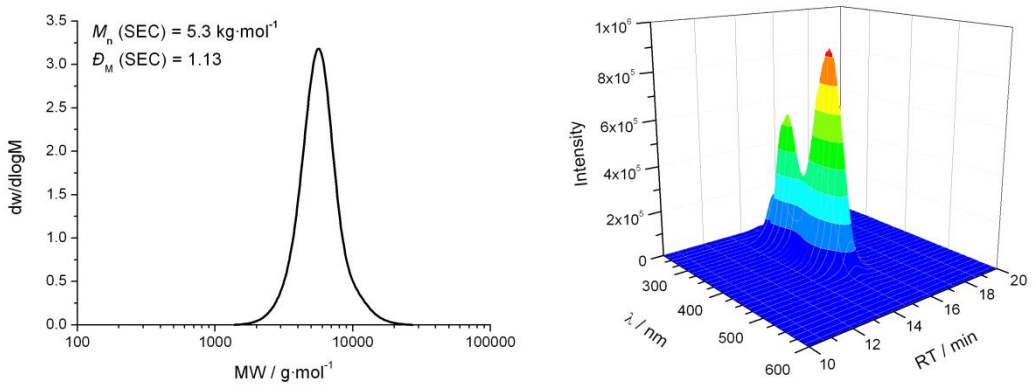


Figure S8. SEC molecular weight distribution (left) and three dimensional SEC chromatogram obtained using a PDA detector (right) for **P1**.

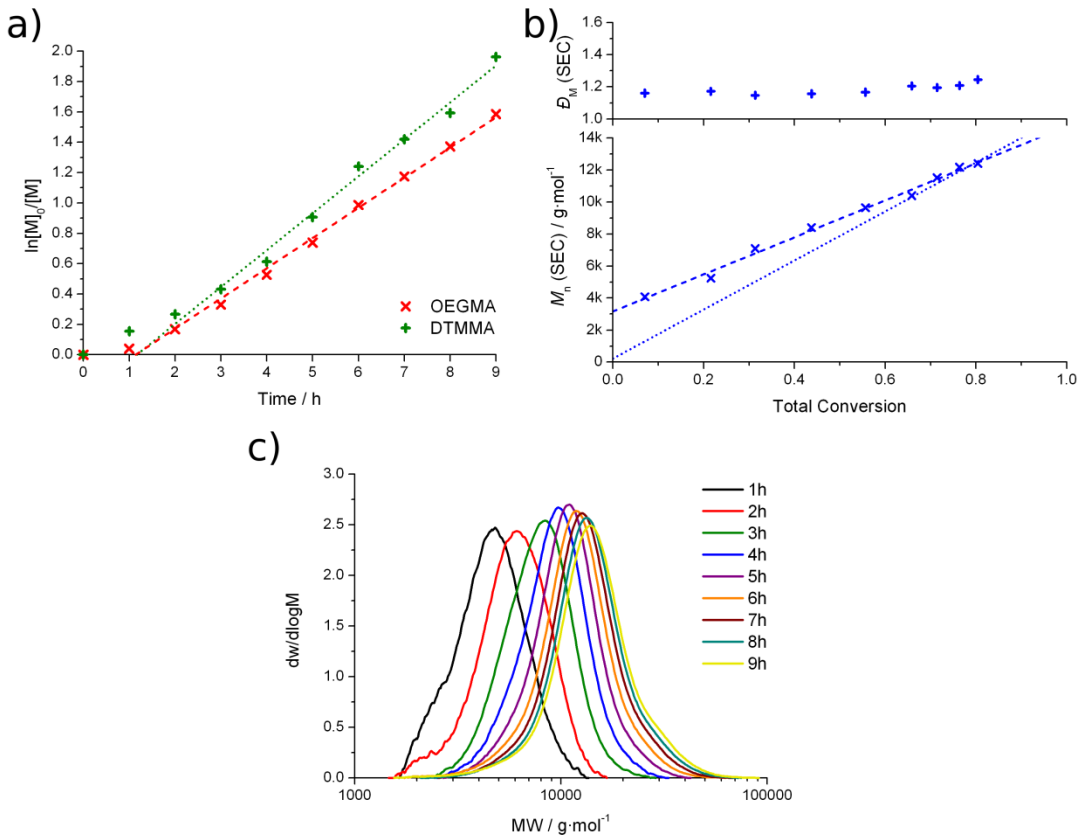


Figure S9. DTMMA/OEGMA copolymerisation **P2**; a) First order kinetics of DTMMA and MMA consumption with linear fits; b) M_n and $Đ_M$ (as measured by SEC) as a function of total monomer conversion with linear fit (dashed line - - -) and theoretical values (assuming equivalent rates of conversion for both monomers, dotted line · · ·); c) Evolution of molecular weight distribution (as measured by SEC) as a function of time.

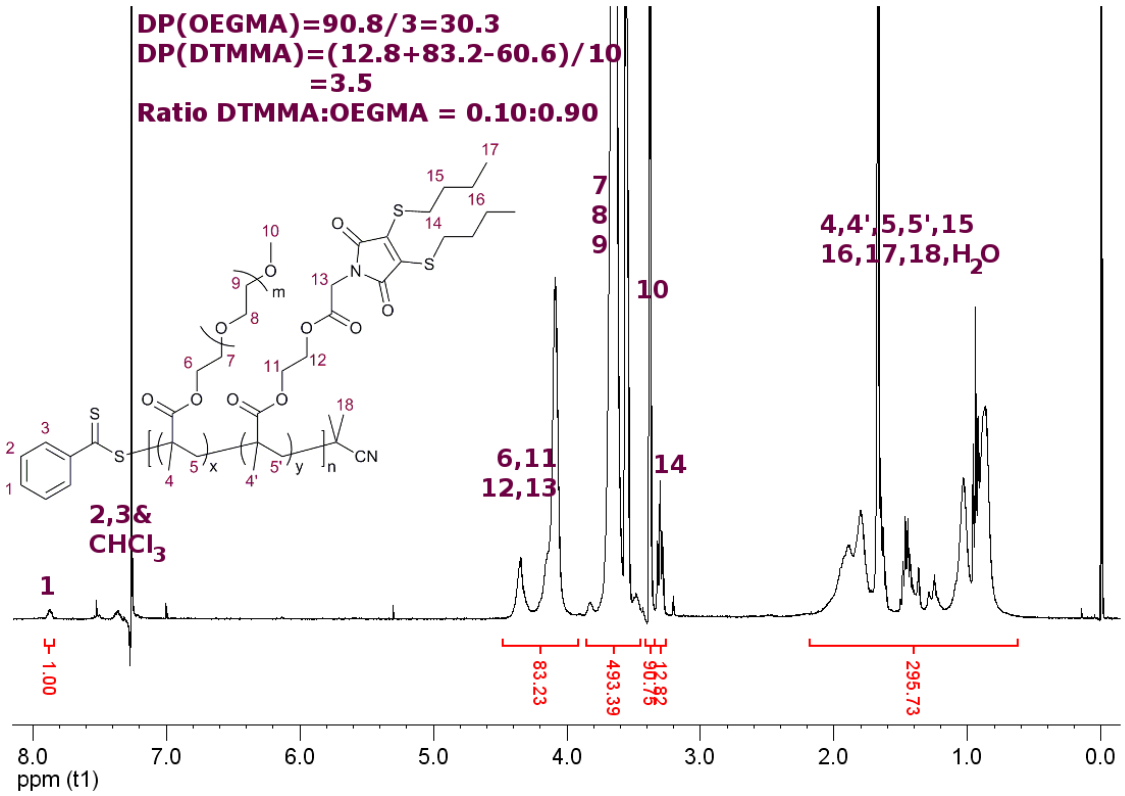


Figure S10. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **P2**.

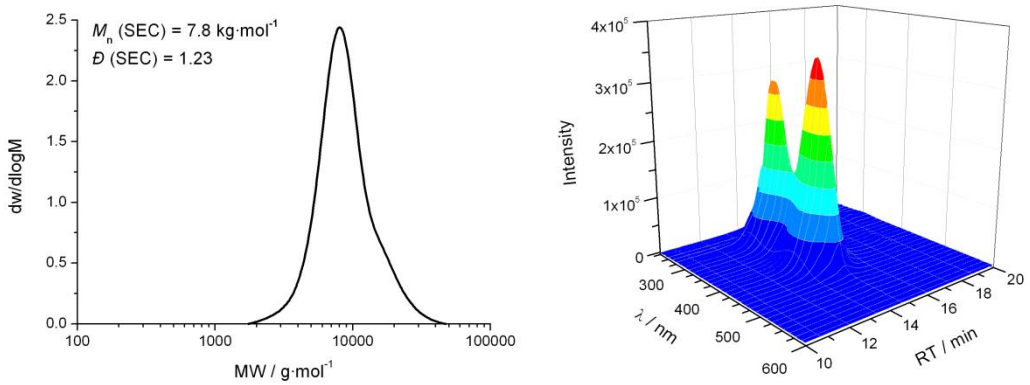


Figure S11. SEC molecular weight distribution (left) and three dimensional SEC chromatogram obtained using a PDA detector (right) for **P2**.

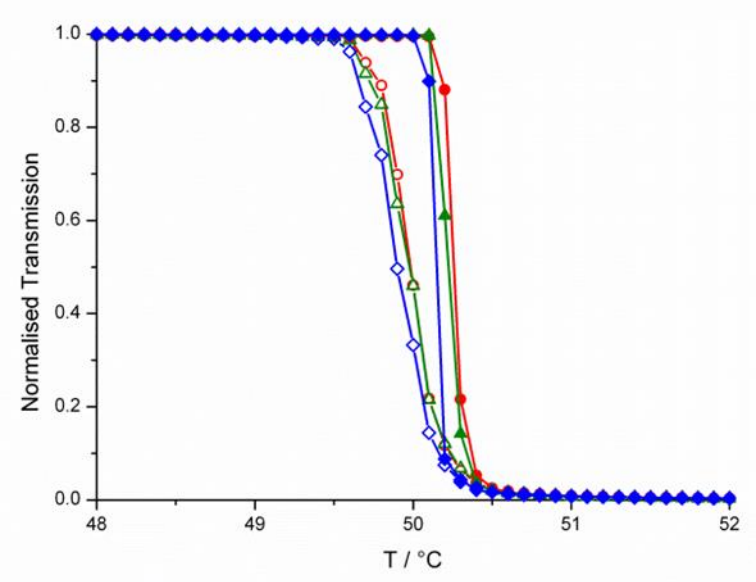


Figure S12. Temperature-dependent light transmission for a solution of **P2** in water (10 g/l). Closed symbols represent heating cycles and open symbols represent cooling cycles.

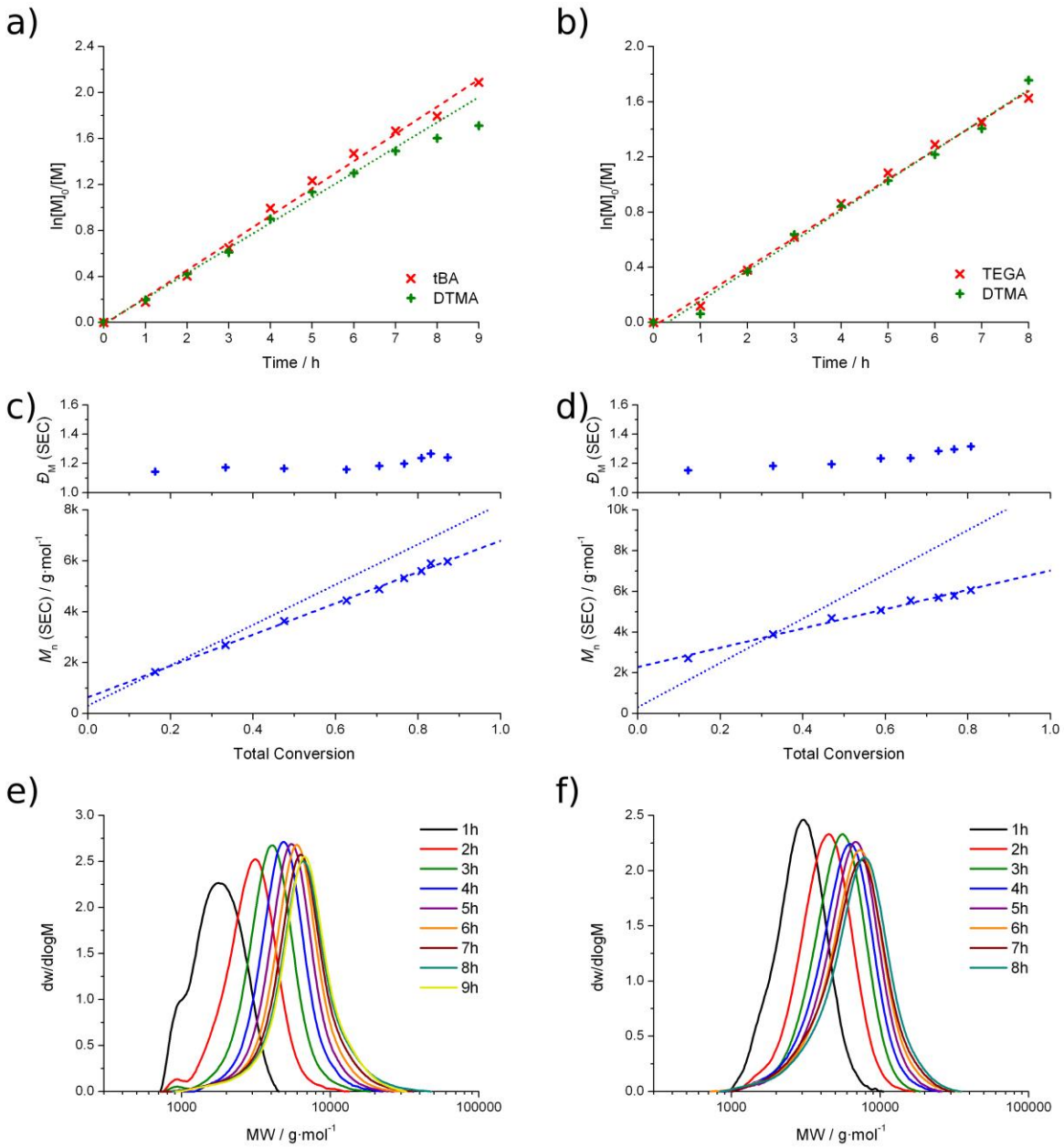


Figure S13. DTMA/tBA copolymerisation **P3** (left) and DTMA/TEGA copolymerisation **P4** (right); a&b) First order kinetics of DTMA and tBA/TEGA consumption with linear fits; c&d) M_n and $Đ_M$ (as measured by SEC) as a function of total monomer conversion with linear fits (dashed lines - - -) and theoretical values (assuming equivalent rates of conversion for both monomers, dotted lines · · ·); e&f) Evolution of molecular weight distribution (as measured by SEC) as a function of time.

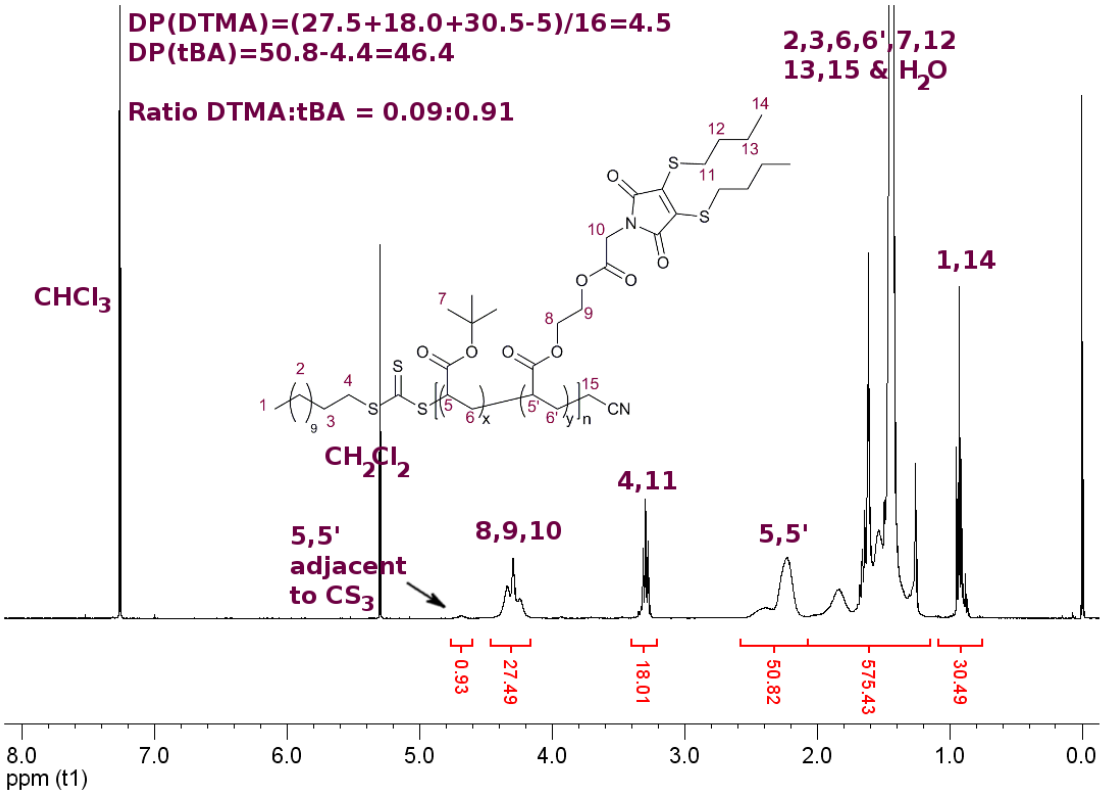


Figure S14. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **P3**.

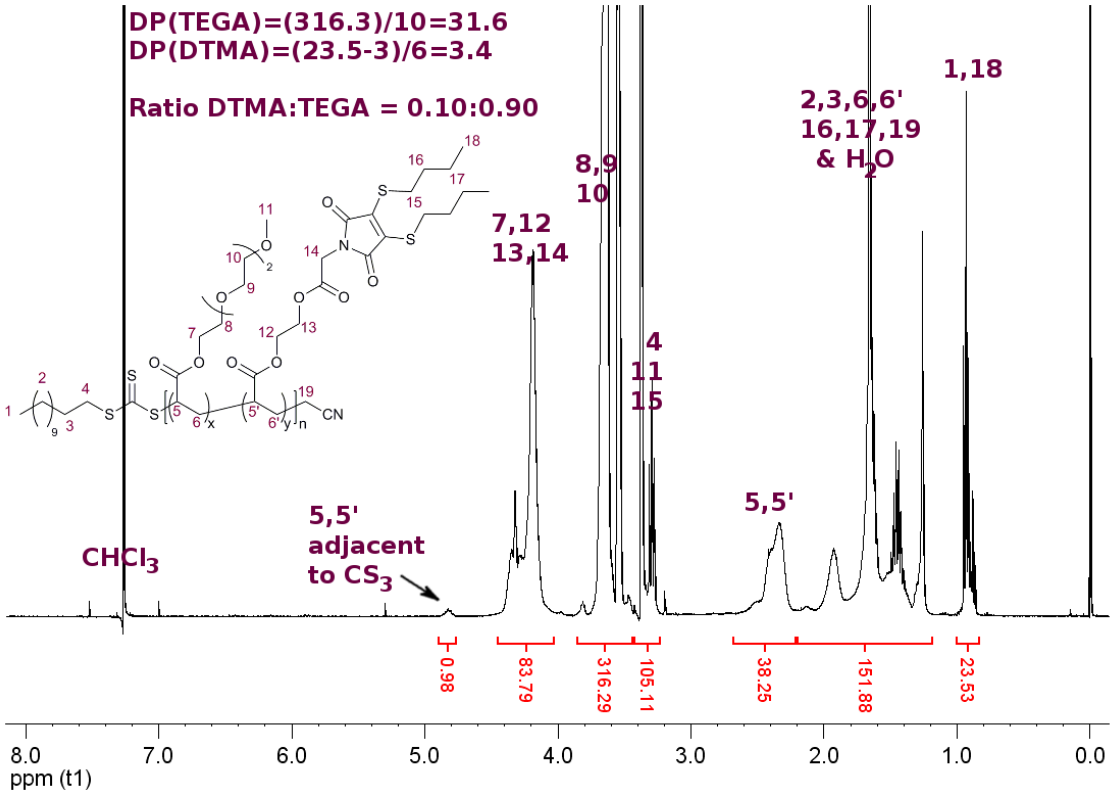


Figure S15. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **P4**.

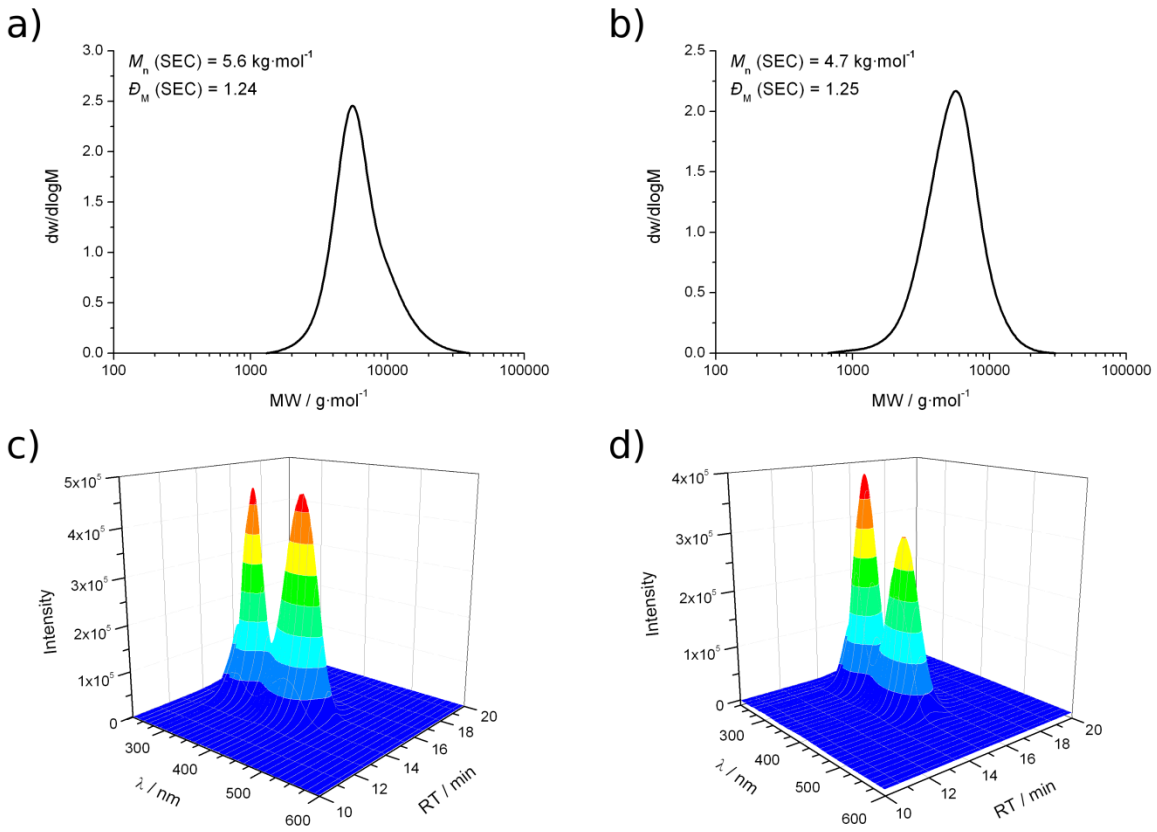


Figure S16. SEC molecular weight distribution of a) **P3**; b) **P4**. Three dimensional SEC chromatogram obtained using a PDA detector for c) **P3**; d) **P4**.

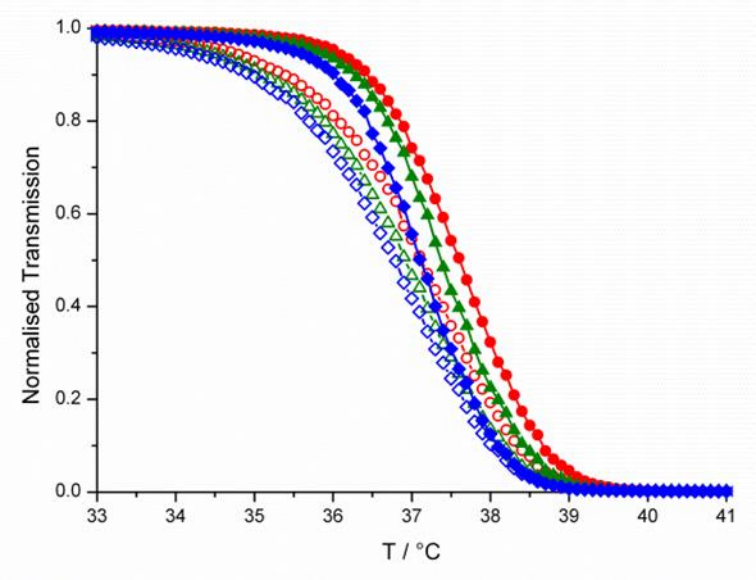


Figure S17. Temperature-dependent light transmission for a solution of **P4** in water (10 g/l). Closed symbols represent heating cycles and open symbols represent cooling cycles.

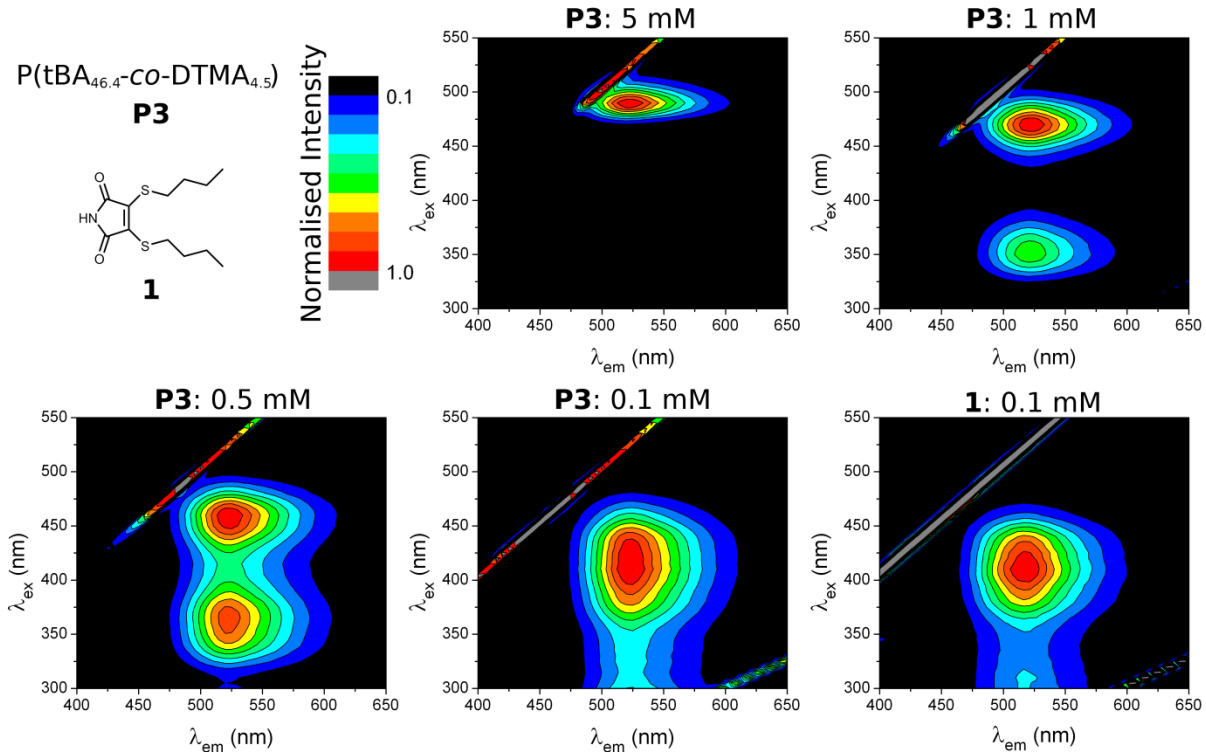


Figure S18. 2D excitation-emission spectra with a 5 nm step for solutions of **P3** and **1** in $CHCl_3$. Aggregate/multimer and dimer emission is seen for P3 at 5, 1 and 0.5 mM, with unimer emission observed for **P3** and **1** at 0.1 mM. Note; for **P3** the concentration given is that of DTM units in solution, with an average of 4.5 DTM units per polymer chain calculated by ^{1}H NMR spectroscopy (see Fig. S14).

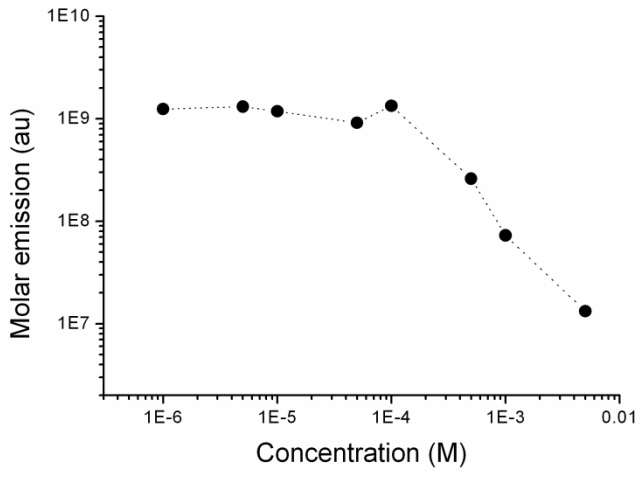


Figure S19. Concentration-based molar emissivity for **P3** in $CHCl_3$.

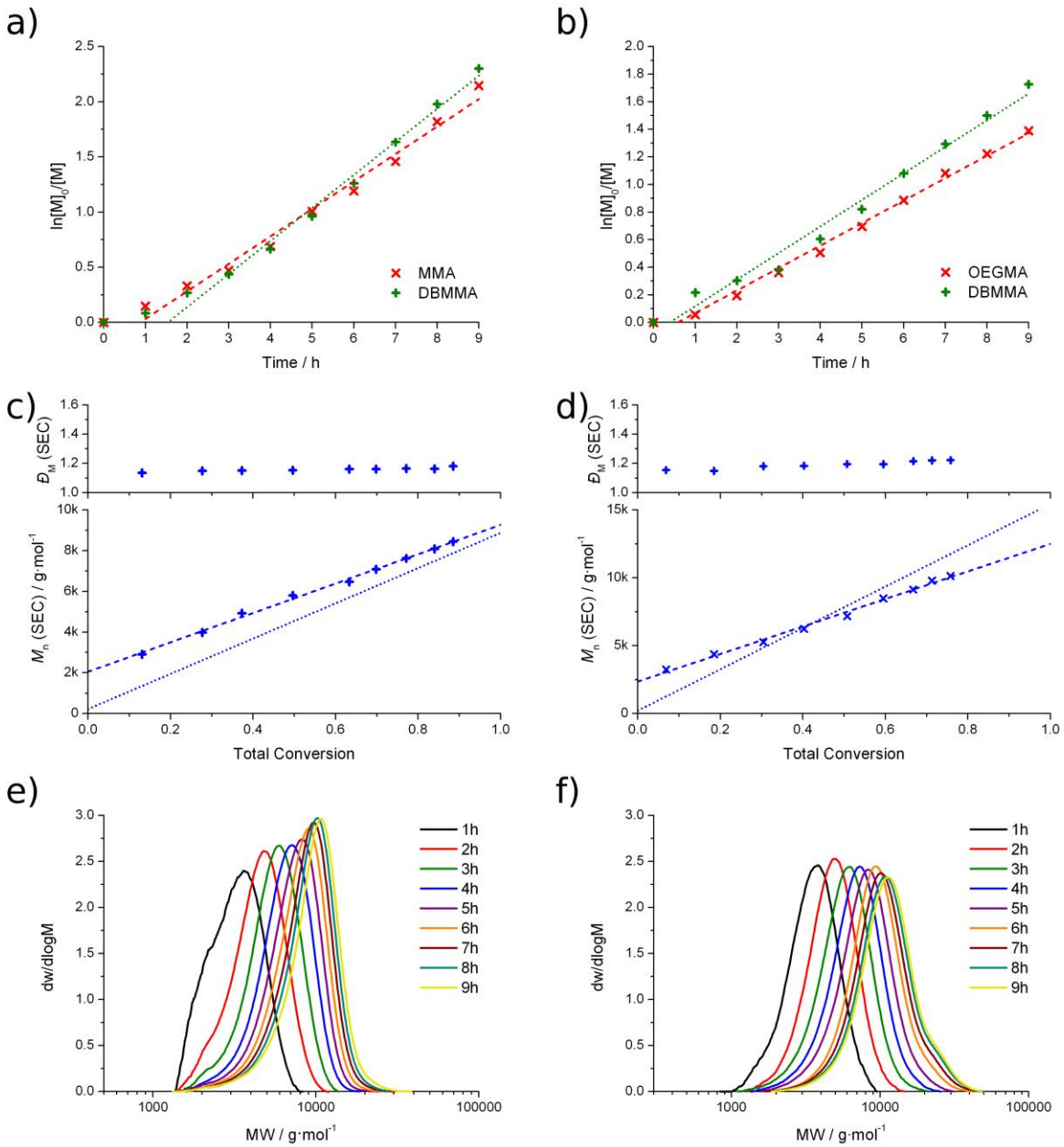


Figure S20. DBMMA/MMA copolymerisation **P5** (left) and DBMMA/OEGMA copolymerisation **P6** (right); a&b) First order kinetics of DBMMA and MMA/OEGMA consumption with linear fits; c&d) M_n and $Đ_M$ (as measured by SEC) as a function of total monomer conversion with linear fits (dashed lines - - -) and theoretical values (assuming equivalent rates of conversion for both monomers, dotted lines · · ·); e&f) Evolution of molecular weight distribution (as measured by SEC) as a function of time.

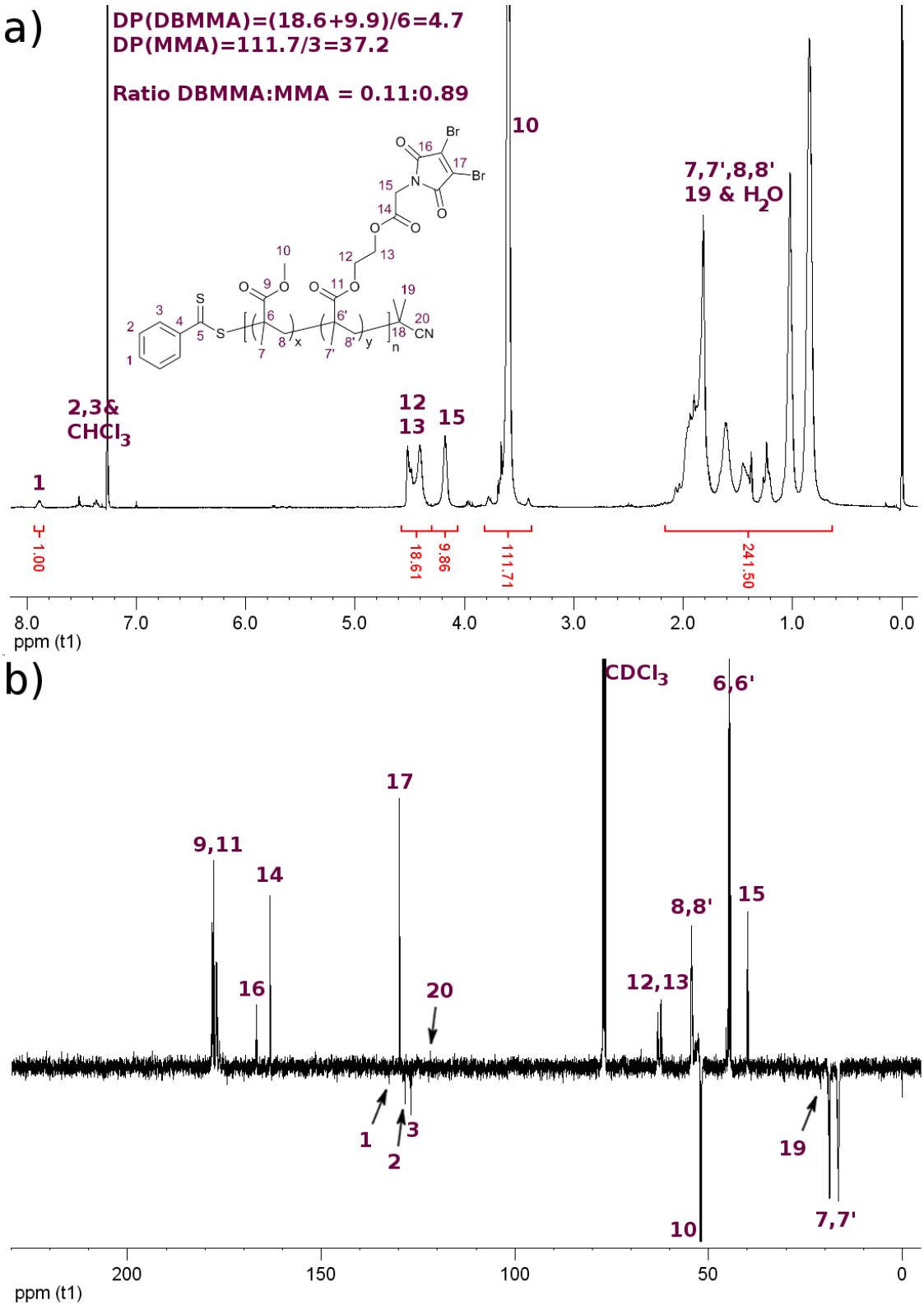


Figure S21. a) ^{1}H NMR (400 MHz, $CDCl_3$) spectrum and b) ^{13}C NMR (125 MHz, $CDCl_3$) spectrum for **P5**. The quaternary end-group carbons C4, C5 and C18 were not observed.

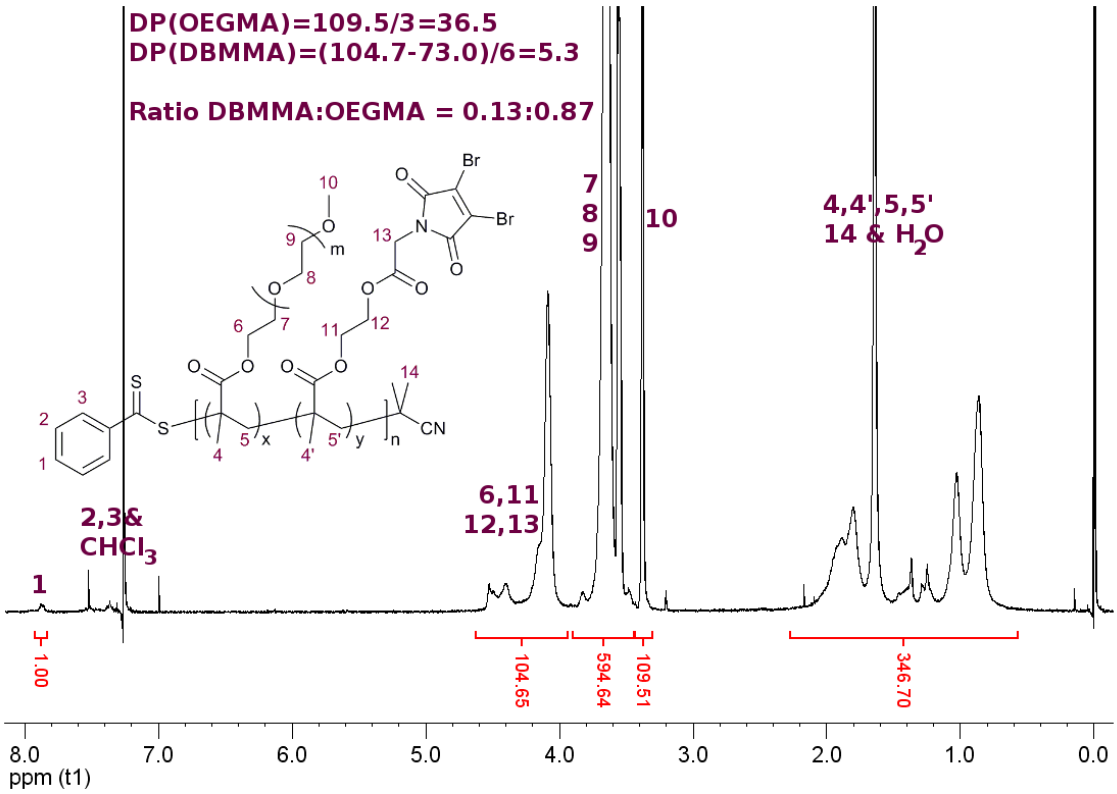


Figure S22. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **P6**.

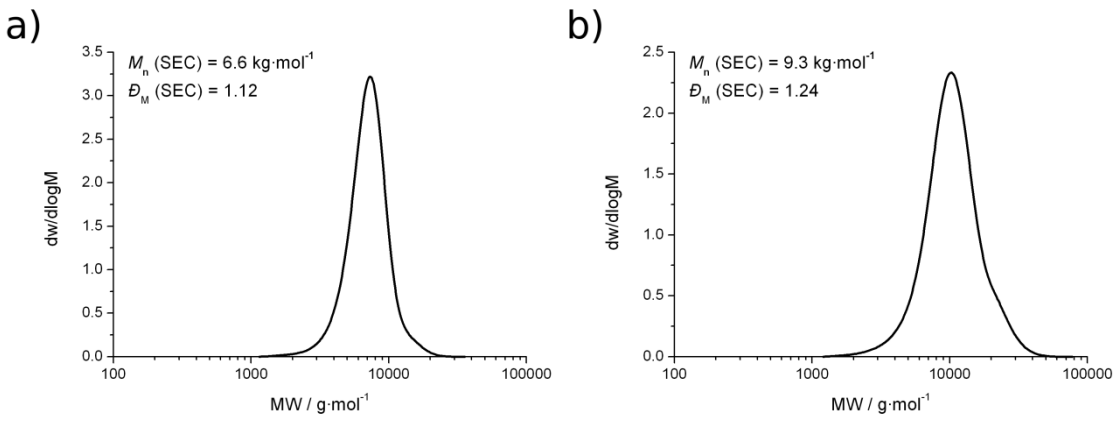


Figure S23. SEC molecular weight distribution of a) **P5**; b) **P6**.

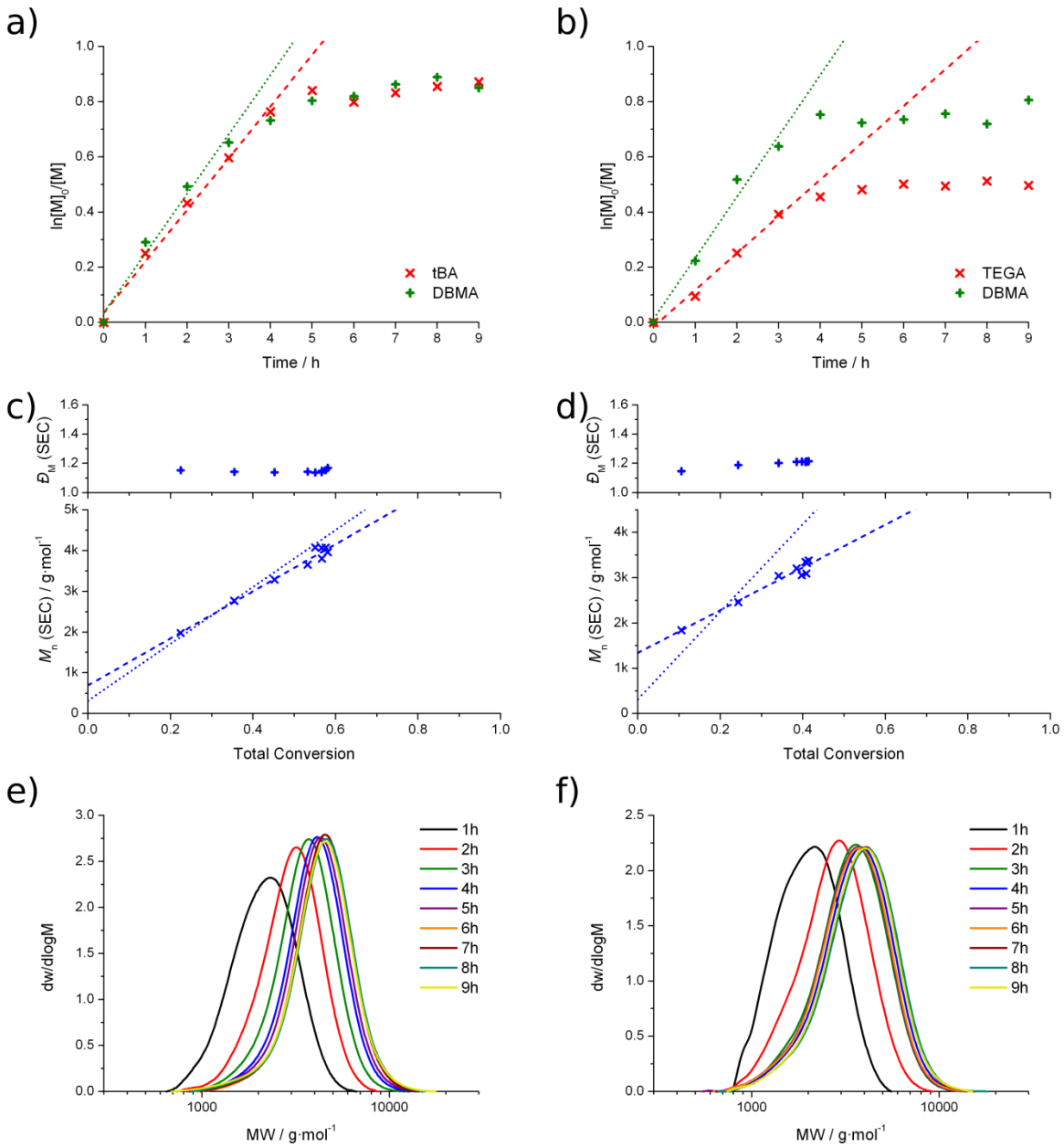


Figure S24. DBMA/tBA copolymerisation **P7** (left) and DBMA/TEGA copolymerisation **P8** (right); a&b) First order kinetics of DBMA and ^{t}BA/TEGA consumption with linear fits to the initial rate; c&d) M_n and $Đ_M$ (as measured by SEC) as a function of total monomer conversion with linear fits (dashed line - - -) and theoretical values (assuming equivalent rates of conversion for both monomers, dotted lines · · ·); e&f) Evolution of molecular weight distribution (as measured by SEC) as a function of time.

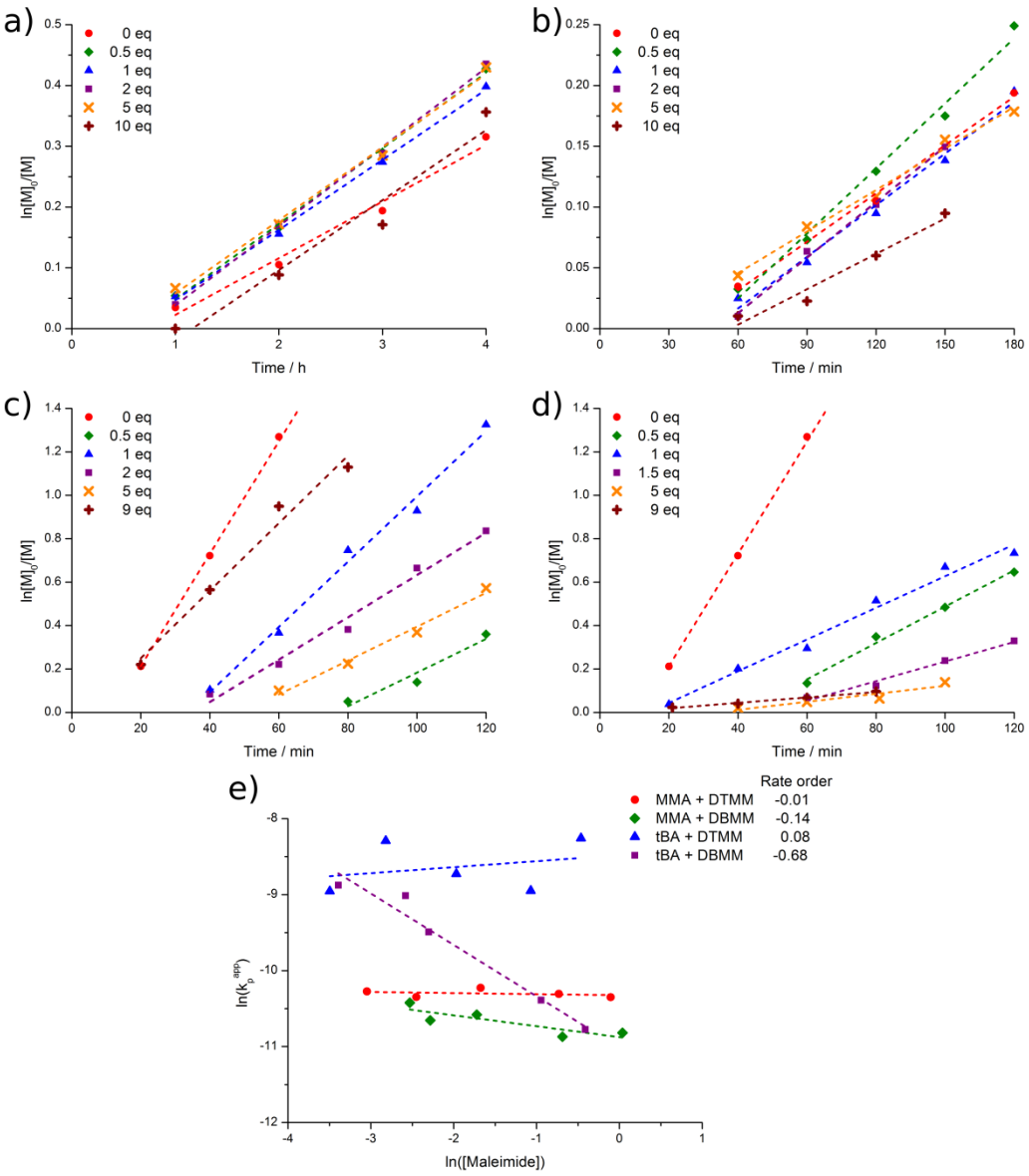


Figure S25. First order kinetics of monomer consumption for RAFT polymerisations in the presence of dibromo or dithiomaleimide. a) MMA and DTMM; b) MMA and DBMM; c) tBA and DTMM; d) tBA and DBMM. e) Determination of the external orders of reaction for the maleimides DTMM and DBMM.

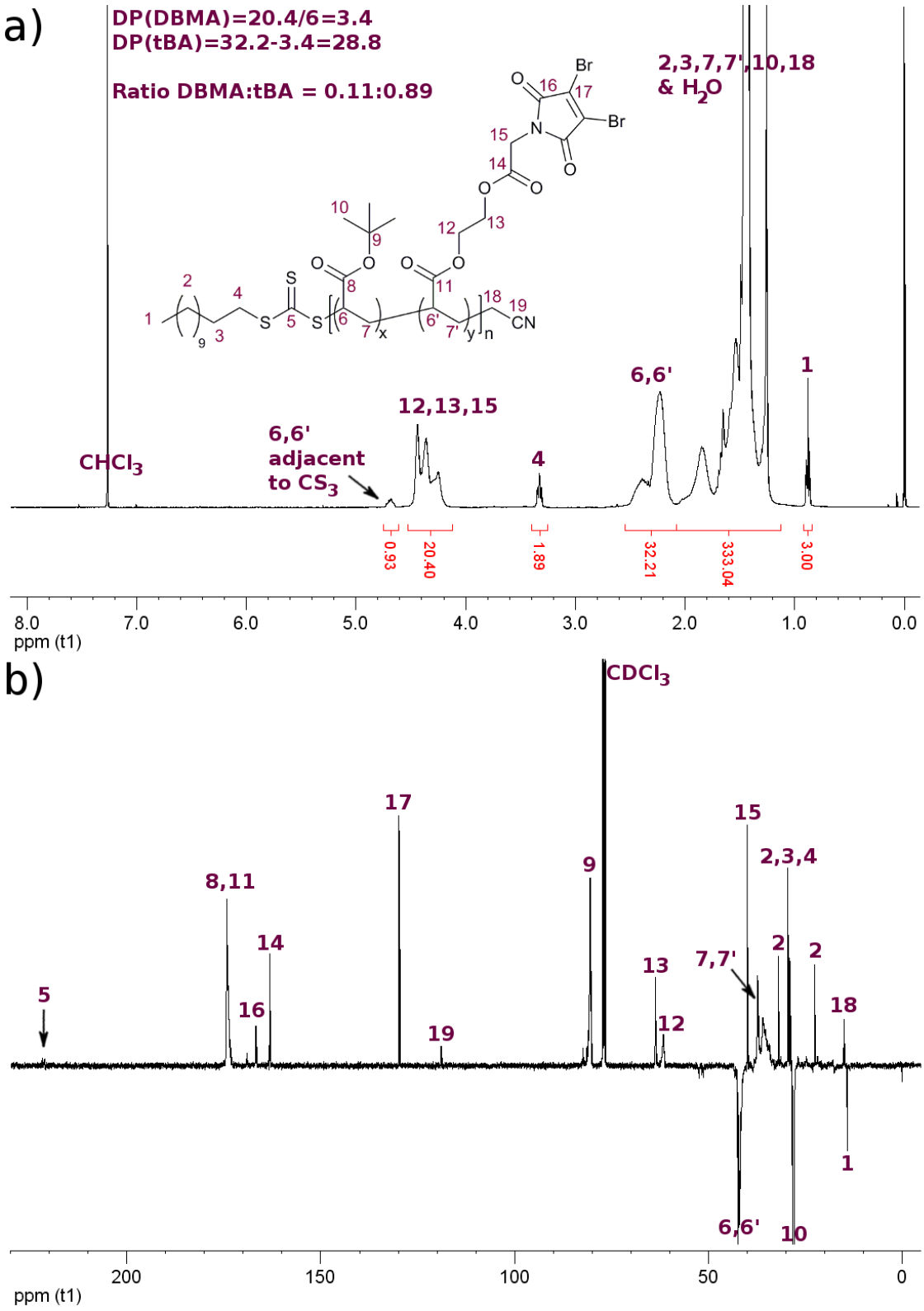


Figure S26 a) ^{1}H NMR (400 MHz, $CDCl_3$) spectrum and b) ^{13}C NMR (125 MHz, $CDCl_3$) spectrum for **P7**.

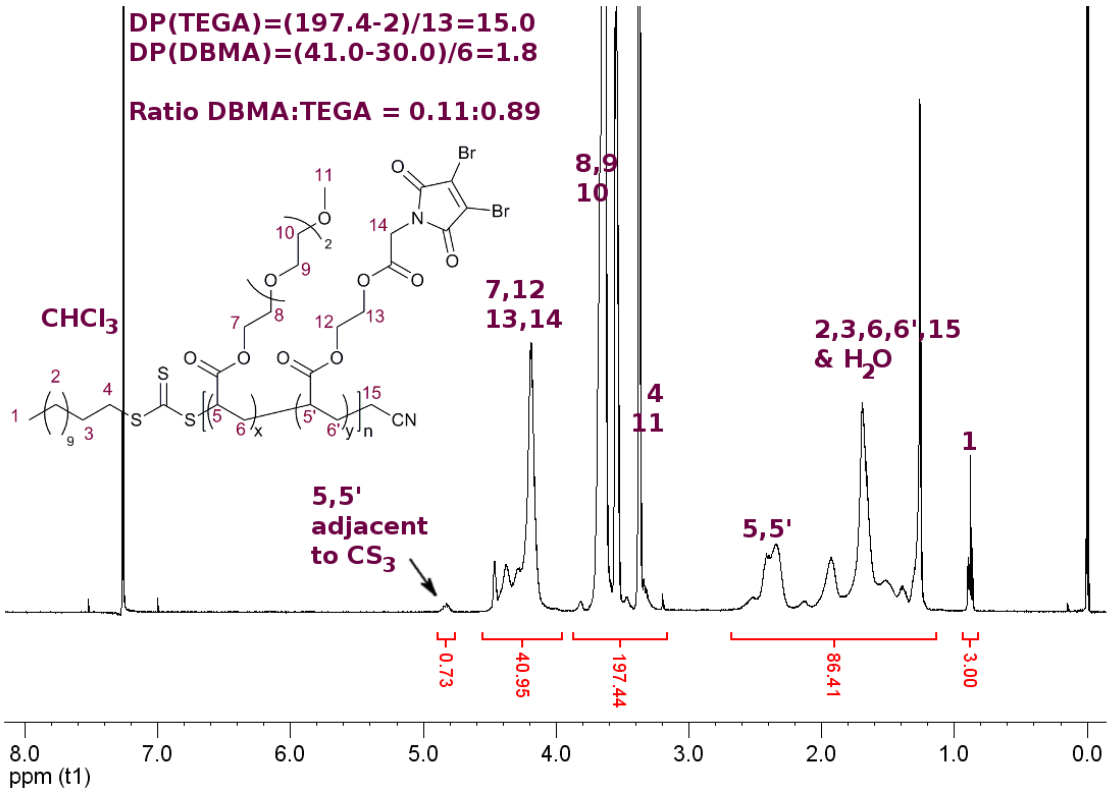


Figure S27. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **P8**.

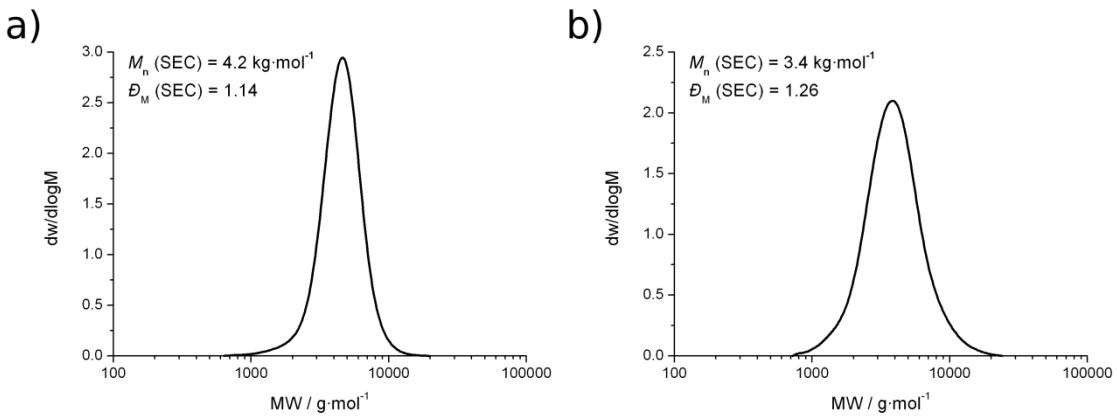
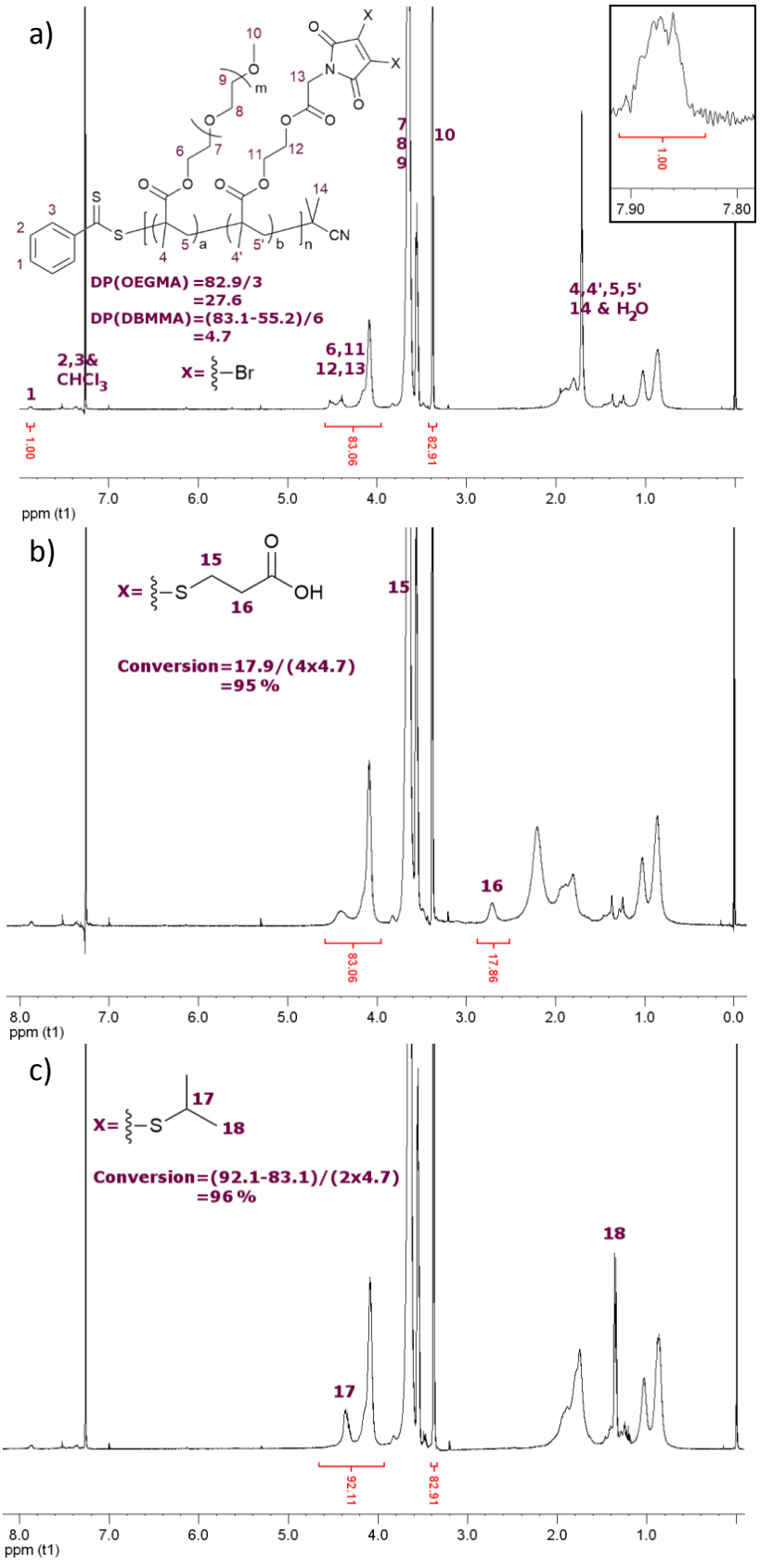


Figure S28. SEC molecular weight distribution of a) **P7**; b) **P8**.


a)
DP(OEGMA) =82.9/3
=27.6
DP(DBMMA)=(83.1-55.2)/6
=4.7
2,3&
CHCl3
X=
Br
6,11
12,13
7
8
9
10
4,4',5,5'
14 & H2O
1.00
83.06
82.91
7.90
7.80
ppm (t1)
b)
X=
S
OH
15
16
Conversion=17.9/(4x4.7)
=95 %
17.86
c)
17
18
Conversion=(92.1-83.1)/(2x4.7)
=96 %
92.11

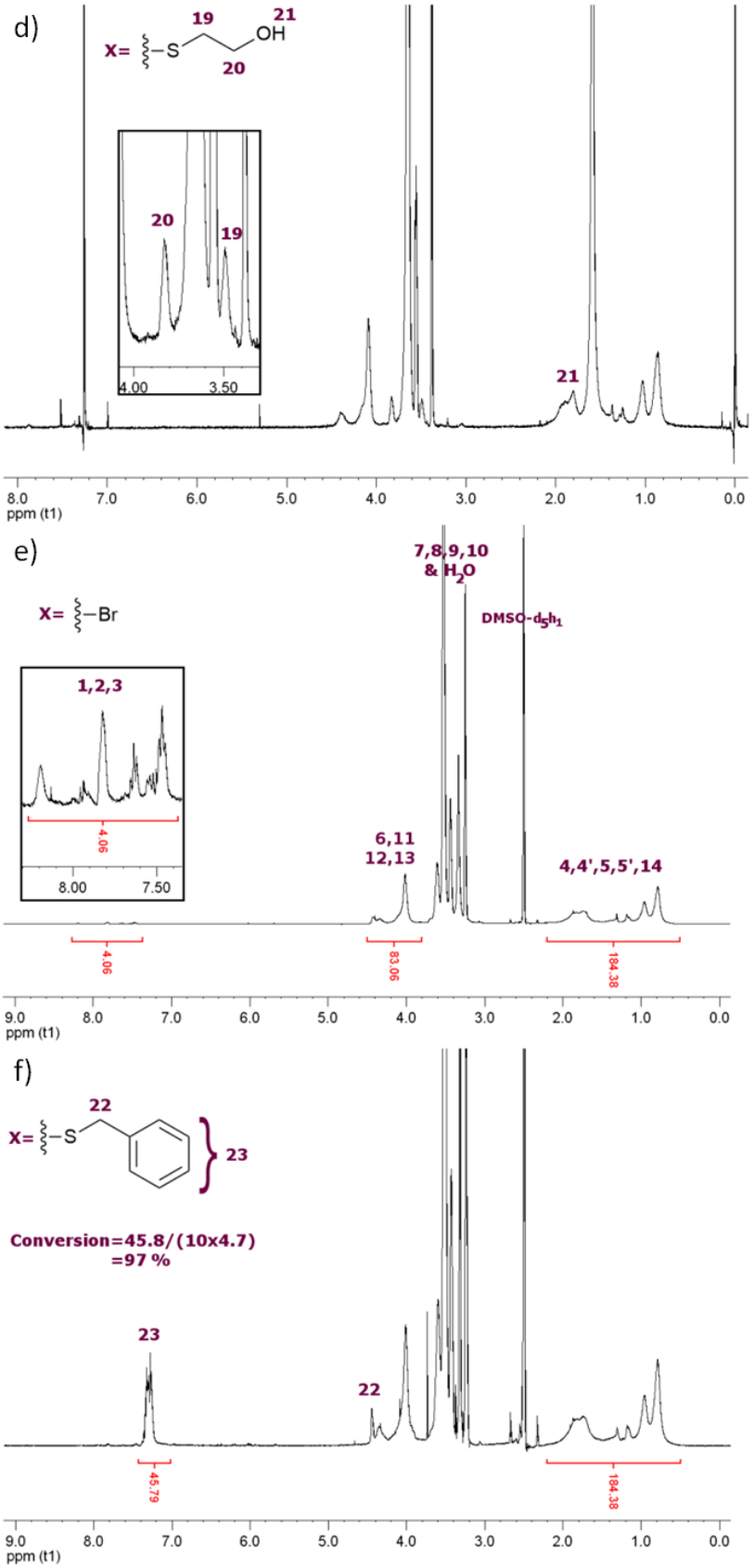


Figure S29. ^{1}H NMR spectra of a) **P11** in $CDCl_3$ and e) **P11** in DMSO-d_6; and the products of the reaction of **P11** with b) $HS(CH_2)_2CO_2H$ in $CDCl_3$; c) $HSCH(CH_3)_2$; d) $HS(CH_2)_2OH$ in $CDCl_3$; and f) HSBn in DMSO-d_6.

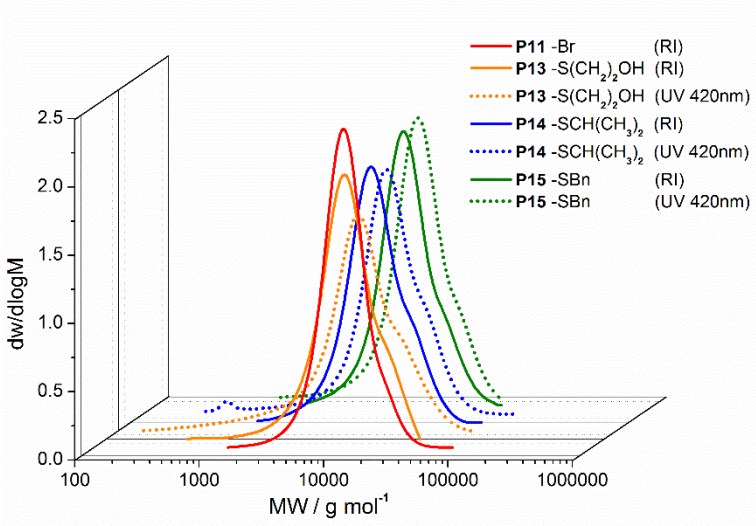


Figure S30. SEC molecular weight distributions for P(OEGMA$_{27.6}$-co-DBMMA$_{4.7}$) (Br), and the products of the post-polymerisation functionalization reaction with various thiols ($S(CH_2)_2OH$, $SCH(CH_3)_2$, SBn, see Table 2 in main text) collected using an RI or UV (λ_{abs} = 420 nm) detectors.

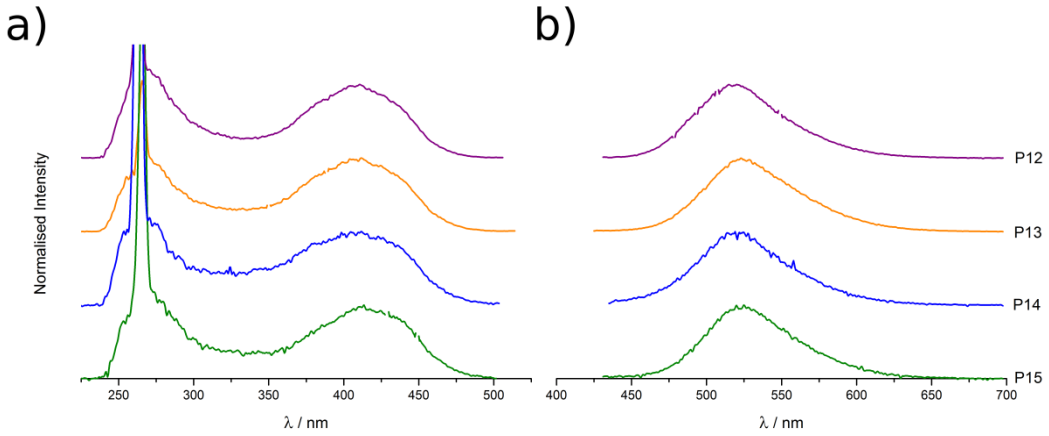


Figure S31. a) Excitation spectra (λ_{em} = 525 nm) and b) Emission spectra (λ_{ex} = 410 nm) for the products of the post-polymerisation functionalization reaction of **P11** with various thiols (**P12**-**15**, see Table 2 in main text) recorded as solutions in chloroform.

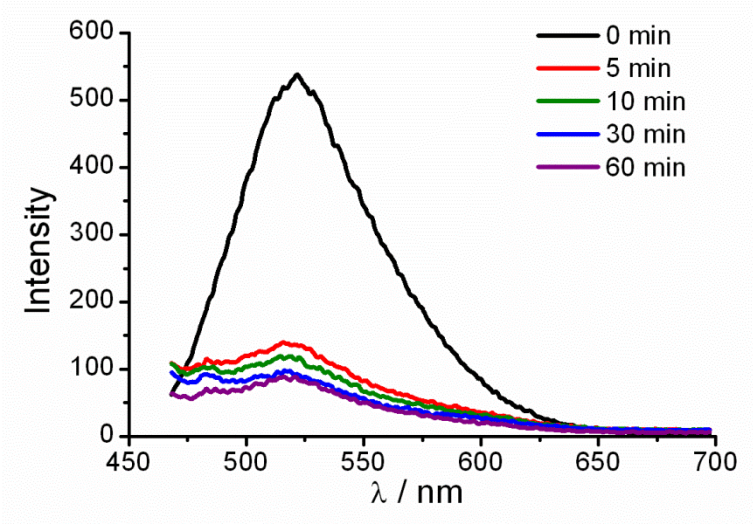


Figure S32. Emission spectra (λ_{ex} = 435 nm) recorded during the reaction of **P4** with thiophenol (to form **P16**) shown in Scheme 4.

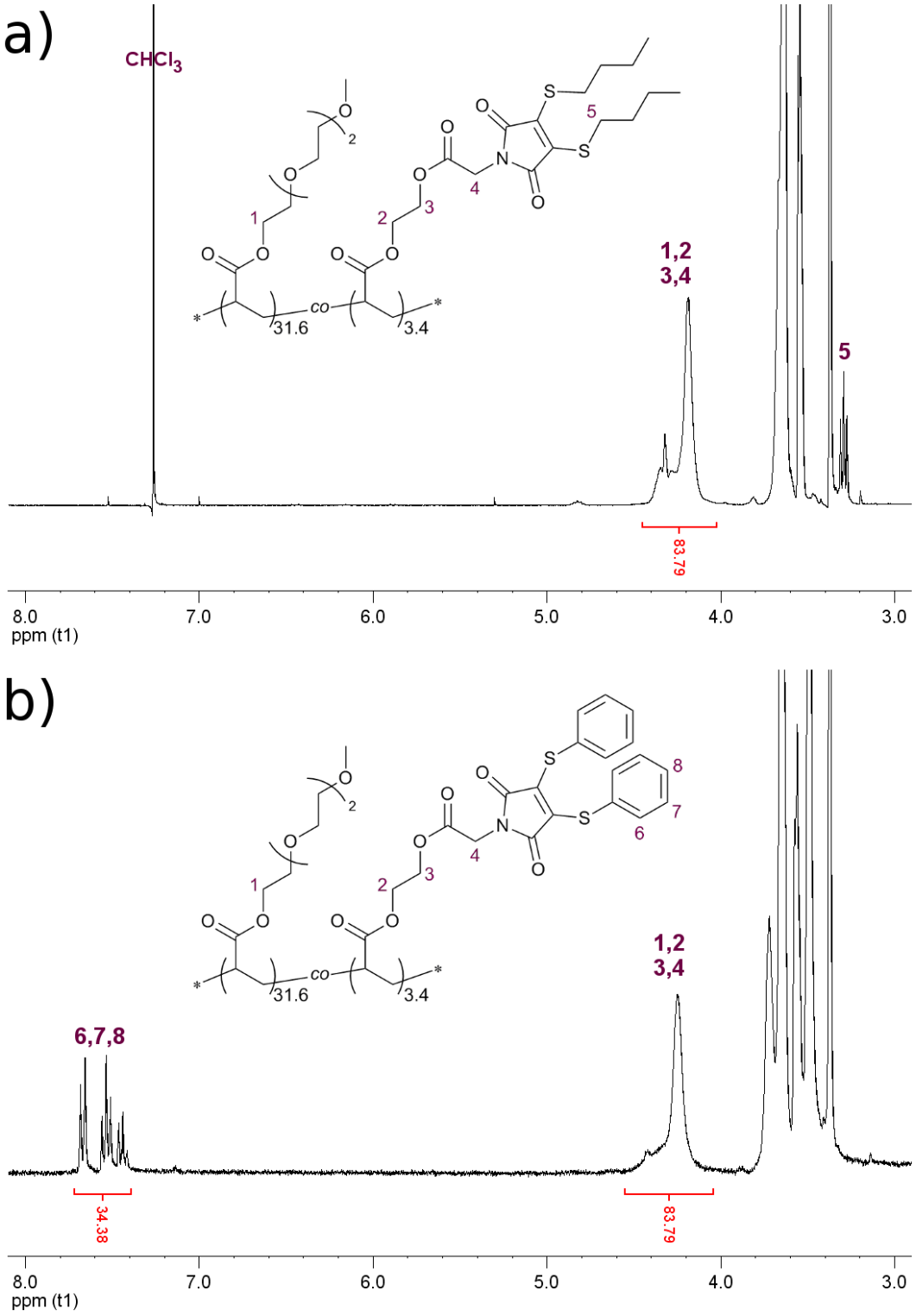


Figure S33 a) Partial ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **P4** and b) Partial ^{1}H NMR (300 MHz, DMSO-d_6) spectrum of **P16**, showing resonances due to DTM thiol ligands.

REFERENCES

1. Y. Kang, A. Lu, A. Ellington, M. C. Jewett and R. K. O'Reilly, *ACS Macro Lett.*, 2013, **2**, 581-586.

2. B. Mu, M. Zhao and P. Liu, *J. Nanopart. Res.*, 2008, **10**, 831-838.

3. M. P. Robin, P. Wilson, A. B. Mabire, J. K. Kiviaho, J. E. Raymond, D. M. Haddleton and R. K. O'Reilly, *J. Am. Chem. Soc.*, 2013, **135**, 2875–2878.

4. F. Hua, X. Jiang, D. Li and B. Zhao, *J. Polym. Sci., Part A: Polym. Chem.*, 2006, **44**, 2454-2467.