Electronic Supplementary Material (ESI) for Polymer Chemistry.

Cleavage of Macromolecular RAFT Chain Transfer Agents by Sodium Azide During Characterization by Aqueous GPC

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Supporting information

Polymer Synthesis

378kDMAT and **365kDMAT** were prepared by a Chemspeed automated parallel synthesiser. In short, degassed standard solutions of AM, APS, NaFS and DMAT were dispensed such that [AM] = 33 wt% and [AM]:[DMAT]:[APS]:[NaFS] = 7000:1:0.125:0.125. The polymerisations were conducted under N_2 at 20^{o}C for 24 hours and samples were analysed without further purification.

7.4kBM1429: AM (8.65 g, 122 mmol), BM1429 (305 mg, 1.2 mmol) and VA-501 (35 mg, 0.12 mmol) were combined with 30 mL of DI water in a round-bottom flask with a condenser. The vessel was then purged with nitrogen for 30 min. before plunging into a 100^{o}C oil bath to react for 2 hours. Quantitative conversion was found by ^{1}H-NMR spectroscopy and the polymer was dried at room temperature (in an open dish) and used without further purification.

18kDBTTC: DMA (17.7 g, 179 mmol), DBTTC (232 mg, 0.80 mmol), Vazo-88 (3.9 mg, 0.016 mmol) and 17 mL MEK were combined in a round-bottom flask and degassed by nitrogen bubbling for 5 minutes. The mixture was then heated in oil bath at 105^{o}C for 2.5 h. Then an additional 20 mL MEK was added and the polymer was precipitated into 250 mL diethyl ether/petroleum spirit (1:1). The polymer was then filtered and washed with diethyl ether then dried in a vacuum oven overnight at 50°C.

10kSPAT: DMA (17.3 g, 175 mmol), SPAT (417 mg, 1.75 mmol), VA-501 (9.8 mg, 0.035 mmol) and 17.4 g DI water were combined in a round-bottom flask and degassed by nitrogen bubbling for 5 minutes before polymerising in an oil bath at 100°C for 20 min. The water was removed by freeze drying and the polymer isolated by precipitation from acetone into diethyl ether. The polymer was then filtered and dried in a vacuum oven for 2 days at 50°C.

1.5kDMAT: DMA (980 mg, 9.9 mmol), DMAT (195 mg, 0.69 mmol) and AIBN (4 mg, 0.024 were combined in a round-bottom flask. This was then degassed by nitrogen bubbling for 5 minutes before plunging into an oil bath at 75°C for 100 minutes. The polymer was precipitated from acetone into diethyl ether, filtered and dried under vacuum at room temperature for 2 days.

4.6kCDMPC: DMA (5 g, 50.4 mmol), CDMPC (177 mg, 0.84 mmol), VA-501 (7 mg, 0.025 mmol) and 10mL acetonitrile were combined in a round-bottom flask and degassed by nitrogen bubbling for 5 minutes before polymerising in an oil bath at 108°C for 20 minutes. The water was removed by freeze drying and the polymer was isolated by precipitation from acetone into diethyl ether. The polymer was then filtered and dried in vacuum oven for 2 days at 50°C.

5.3kCPDB: DMA (890 mg, 8.98 mmol), CPDB (20 mg, 0.09 mmol), AIBN (1.5mg, 0.009 mmol) and 3 mL of acetonitrile were combined in a round bottom flask. This was then degassed by nitrogen bubbling for 15 minutes before plunging into an oil bath at 75°C for 44 hours. An additional 2 mg (0.012 mmol) AIBN was added during the course of polymerisation (due to heavy inhibition). The residual acetonitrile was removed by rotary evaporation and the polymer was redissolved in acetone to precipitate into diethyl ether (twice). The polymer was then filtered and dried under vacuum at room temperature for 2 days.

1kXA1: AM (4 g, 56.3 mmol), XA01 (1.67 g, 7.98 mmol), VA-501 (90 mg, 0.32 mmol), 6 mL ethanol and 4.5 mL DI water were combined in a round-bottom flask and then degassed with nitrogen bubbling for 5 minutes before polymerising in an oil bath at 70°C for 70 minutes. The polymer was precipitated into acetone, filtered and dried under vacuum at 50°C for 2 days.

Table S1. Molecular weights and dispersities of selected polymers samples as prepared in various GPC solvents.

Polymer Sample	$M_{n,conv}$ (kDa)	*DI water*		*GPC solvent (with azide)*		*GPC solvent (no azide)*		*200ppm azide*	
		$M_{n,GPC}$ (kDa)	*Đ*	$M_{n,GPC}$ (kDa)	*Đ*	$M_{n,GPC}$ (kDa)	*Đ*	$M_{n,GPC}$ (kDa)	*Đ*
378kDMAT	378	378	1.27	291	1.40	378	12.6	295	1.39
365kDMAT	365	318	1.25	236	1.37	319	1.25	243	1.37
7.4kBM1429	7.4	8.14	1.21	8.24	1.27	8.08	1.22	8.58	1.23

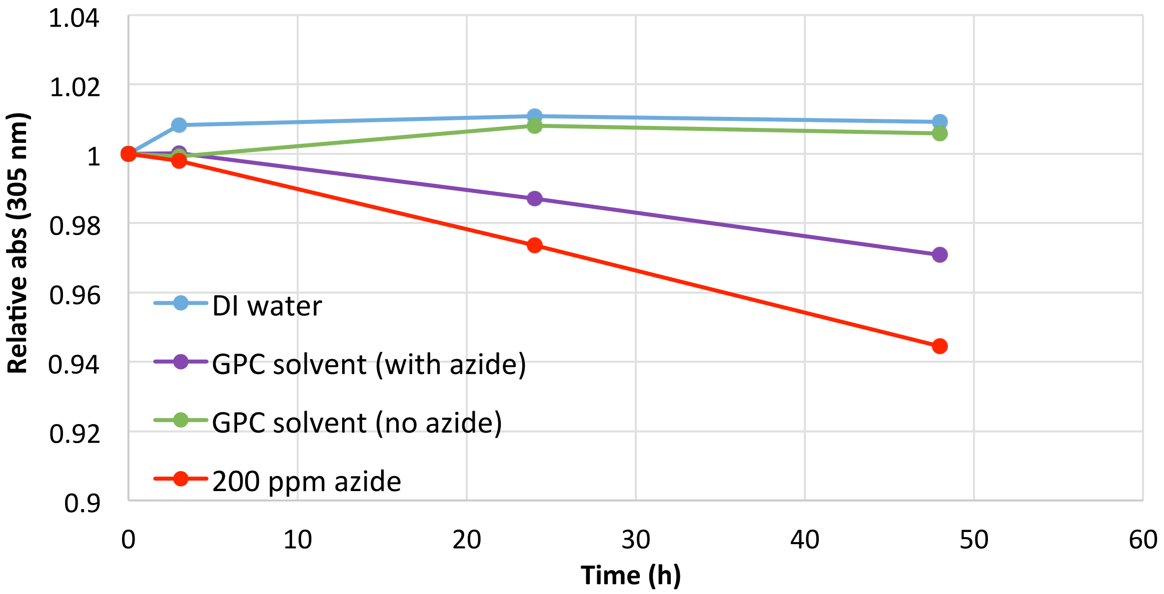

Figure S1. CTA loss of **7.4kBM1429** in different solvents monitored by UV-Vis absorbance at 305 nm (λ_{max} for trithiocarbonates).

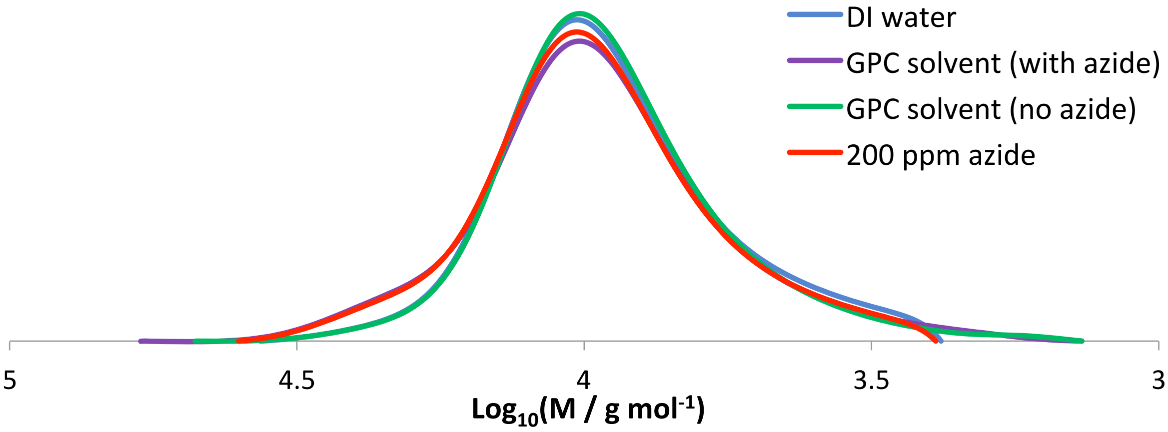

Figure S2. Molecular weight distributions as determined by GPC for **7.4kBM1429** after 48 hours in different solvents.

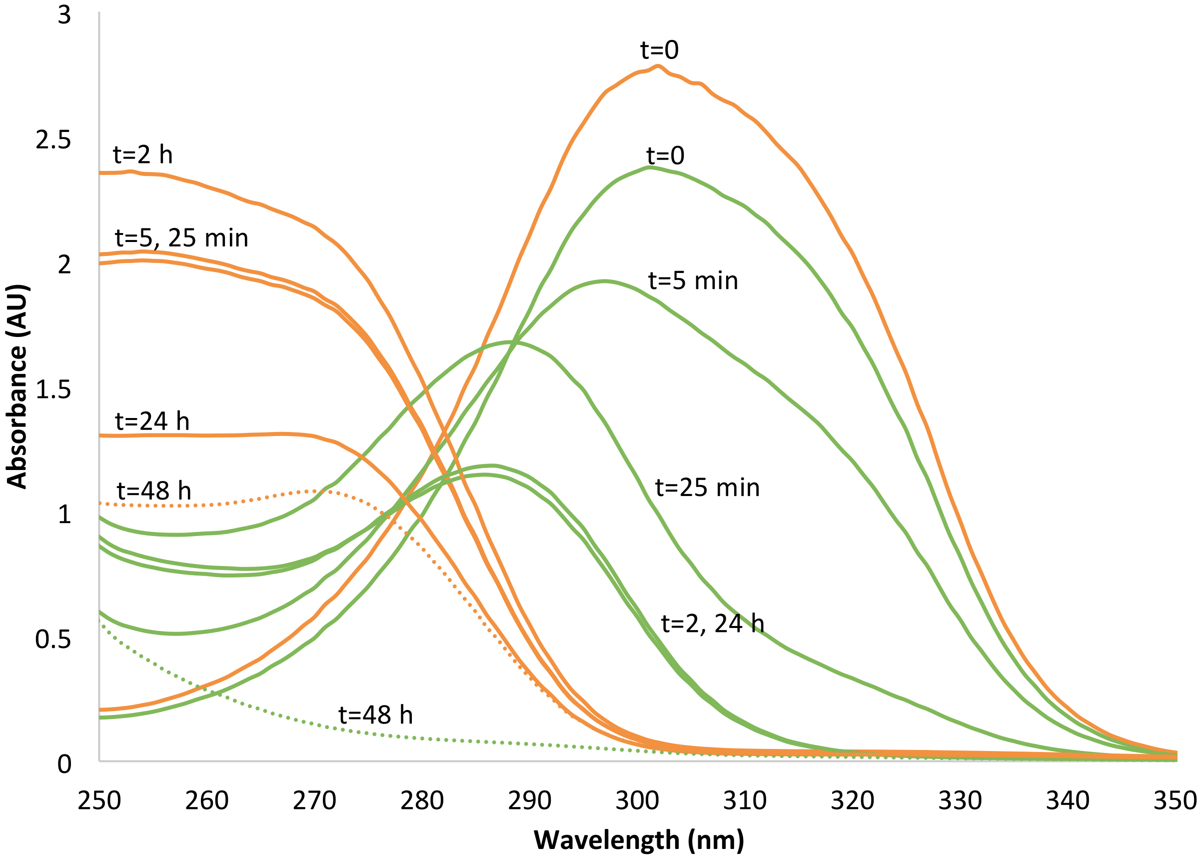

Figure S3. UV-vis spectrum for **4.6kCDMPC** when reacted with 267 mM sodium azide (green) and methylamine (orange). A precipitate was produced during this reaction and the final measurement (taken at 48 hours) is of a filtered sample.

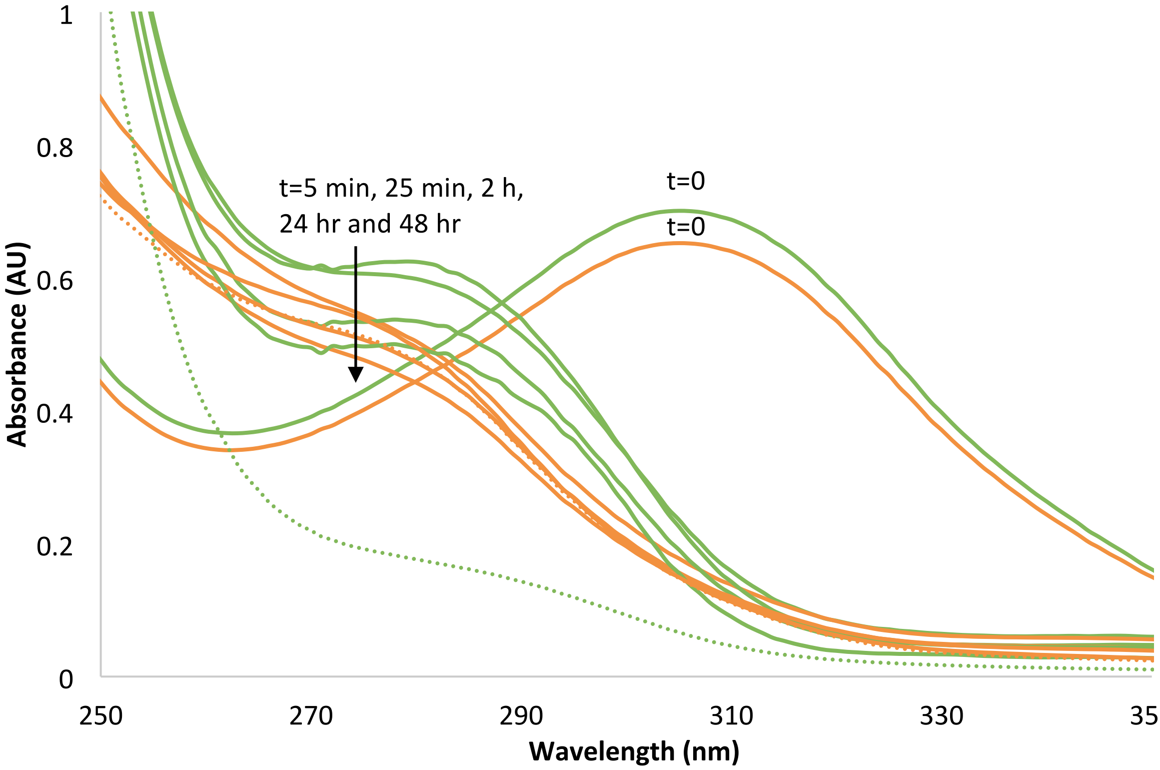

Figure S4. UV-vis spectrum for **5.3kCPDB** when reacted with 267 mM sodium azide (green) and methylamine (orange). A precipitate was produced during this reaction and the final measurement (taken at 48 hours) is of a filtered sample.

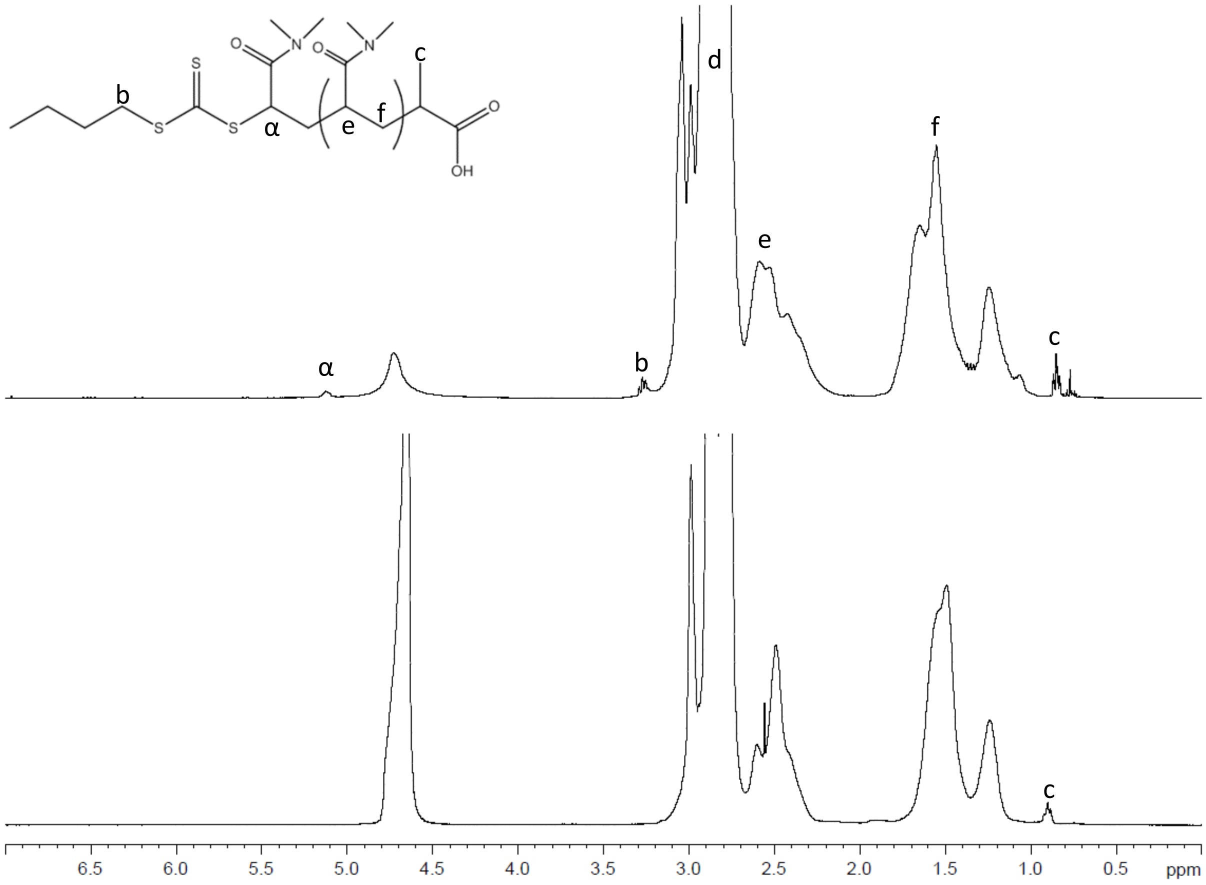

Figure S5. ^{1}H-NMR spectrum of **10kSPAT** polymer before (top, in $CDCl_3$) and after treatment (bottom, in D_2O) with 267 mM sodium azide solution. The α-carbon proton signal (broad, 5.1 ppm) and aliphatic protons from butyl Z group (t, 3.25 ppm) are absent in the water soluble component after treatment with sodium azide, suggesting CTA removal.

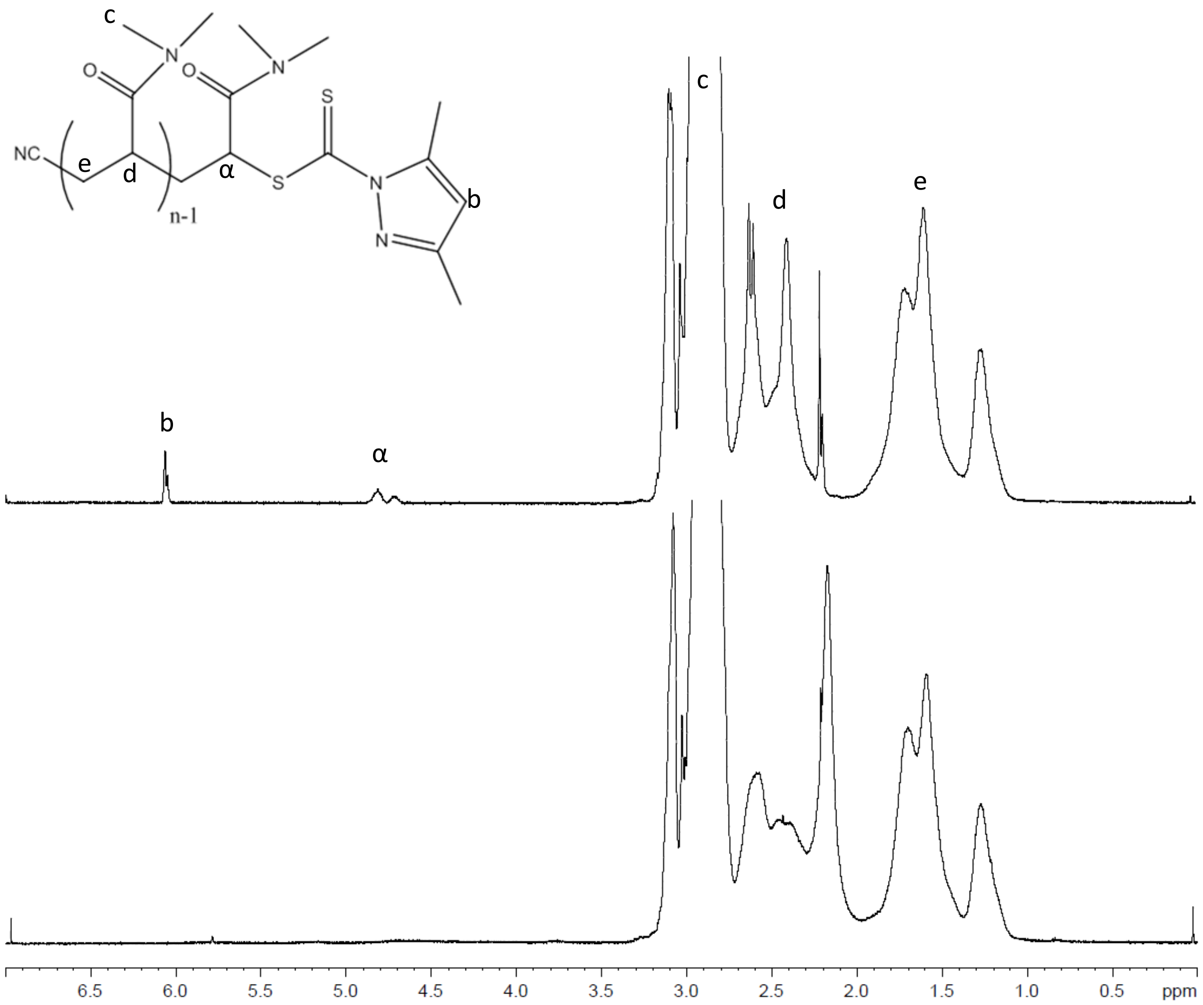

Figure S6. ^{1}H-NMR spectrum of **4.6kCDMPC** polymer before (top, in $CDCl_3$) and after treatment (bottom, in $CDCl_3$) with 267 mM sodium azide solution. The α-carbon proton signal (broad, 4.8 ppm) and pyrazole proton (d, 6.06 ppm) are absent in the water soluble component after treatment with sodium azide, suggesting CTA removal.

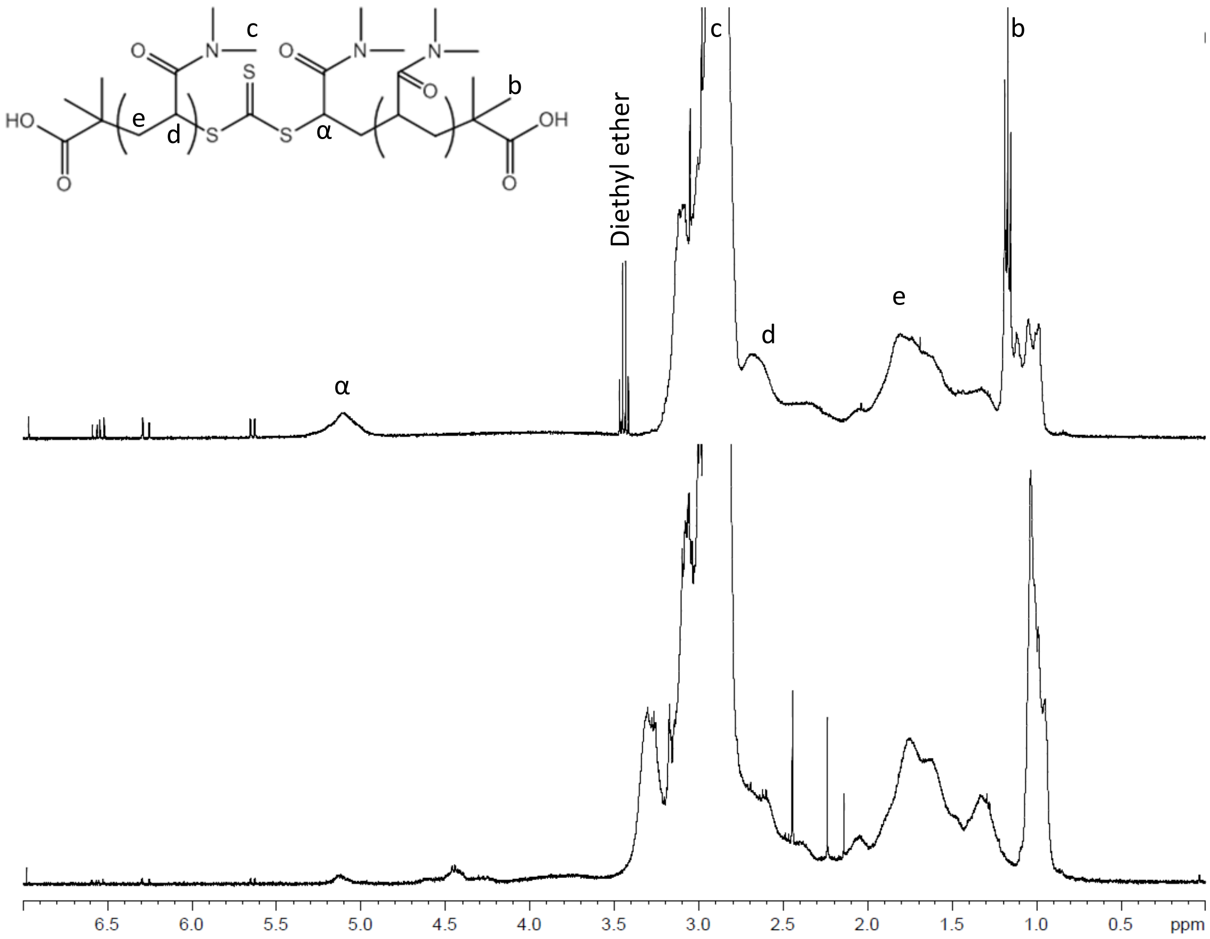

Figure S7. ^{1}H-NMR spectrum of **1.5kDMAT** polymer before (top, in $CDCl_3$) and after treatment (bottom, in $CDCl_3$) with 267 mM sodium azide solution. The α-carbon proton signal (broad, 5.1 ppm) is absent in the water soluble component after treatment with sodium azide, suggesting CTA removal.

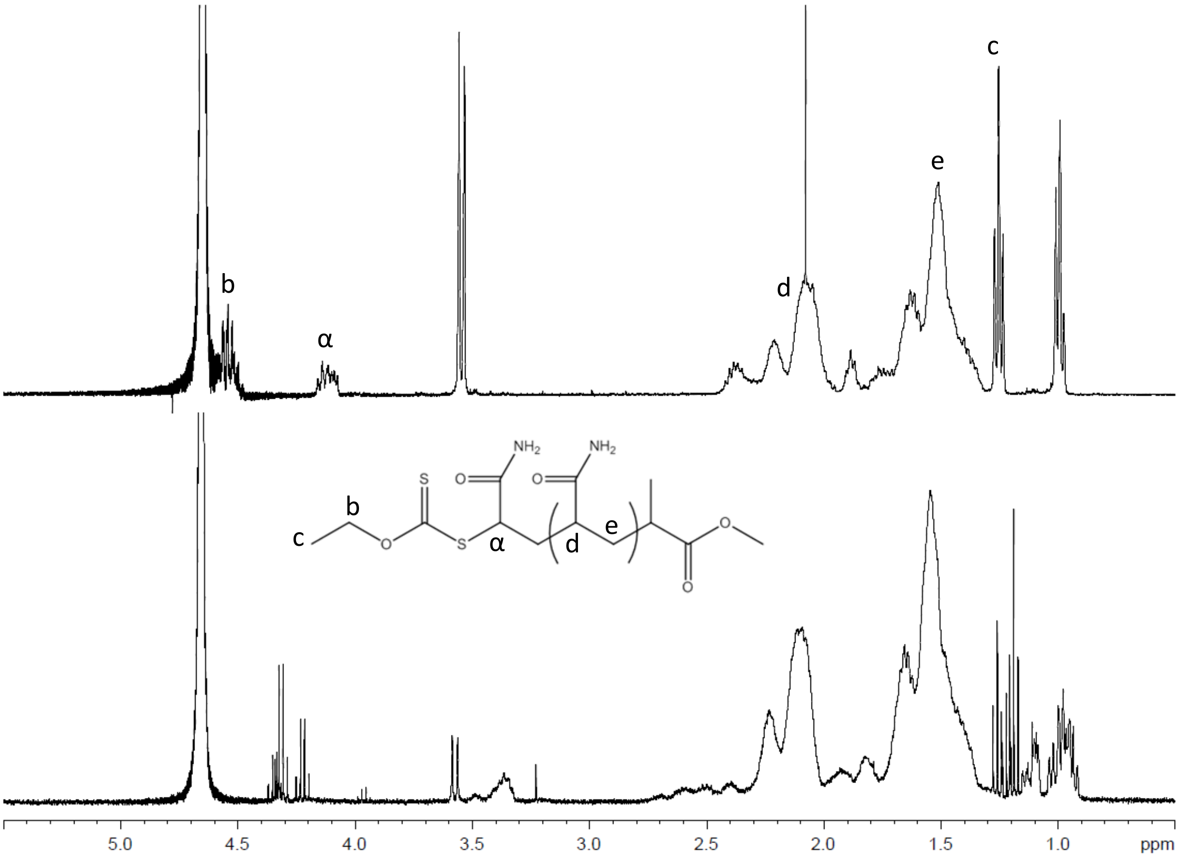

Figure S8. ^{1}H-NMR spectrum of **1kXA1** polymer before (top, in D_2O) and after treatment (bottom, in D_2O) with 267 mM sodium azide solution. The α-carbon proton signal (m, 4.1 ppm) is absent in the water soluble component after treatment with sodium azide, suggesting CTA removal.

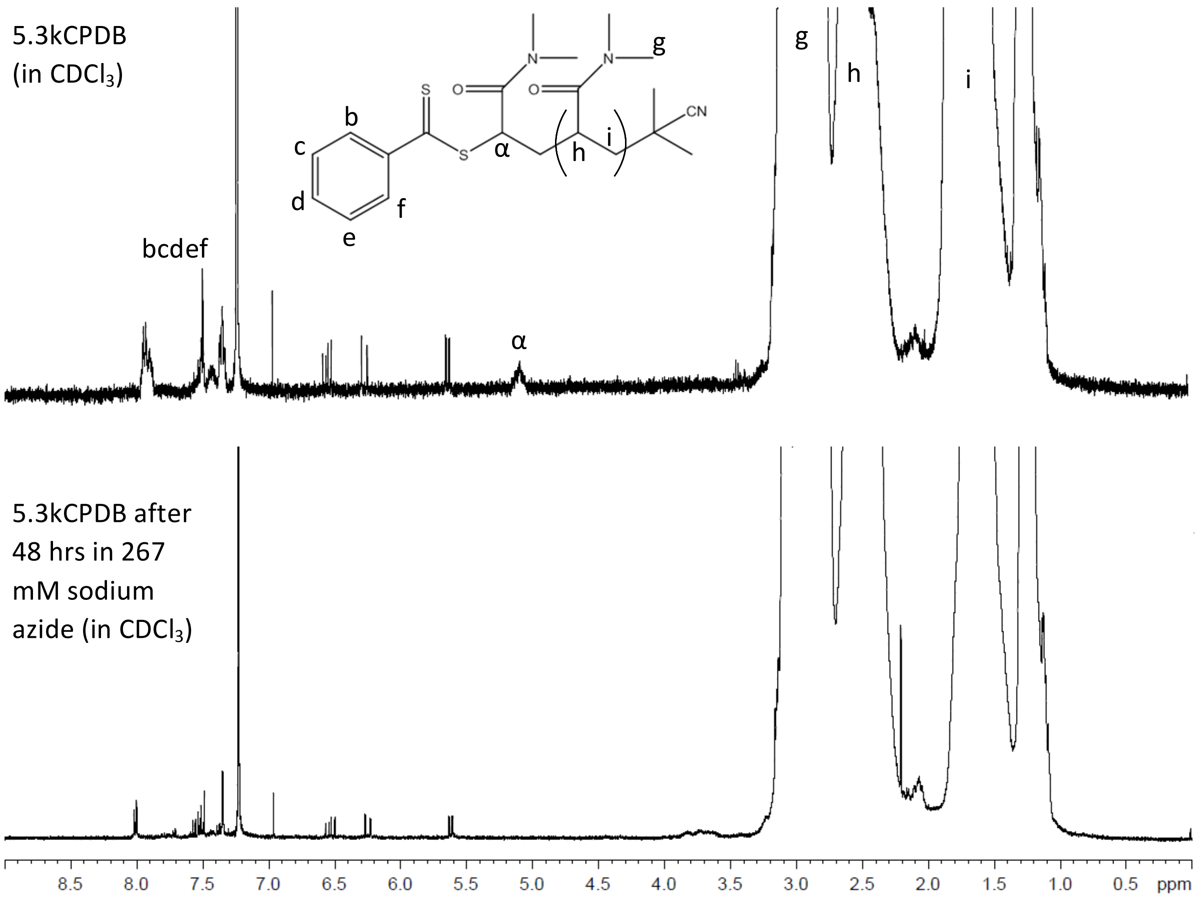

Figure S9. ^{1}H-NMR spectrum of **5.3kCPDB** polymer before (top, in CDCl$_3$) and after treatment (bottom, in CDCl$_3$) with 267 mM sodium azide solution. The α-carbon proton signal (broad, 5.1 ppm) is while and the aromatic Z group protons (7.3 – 8 ppm) are shifted and reduced in the water soluble component after treatment with sodium azide, suggesting CTA removal.

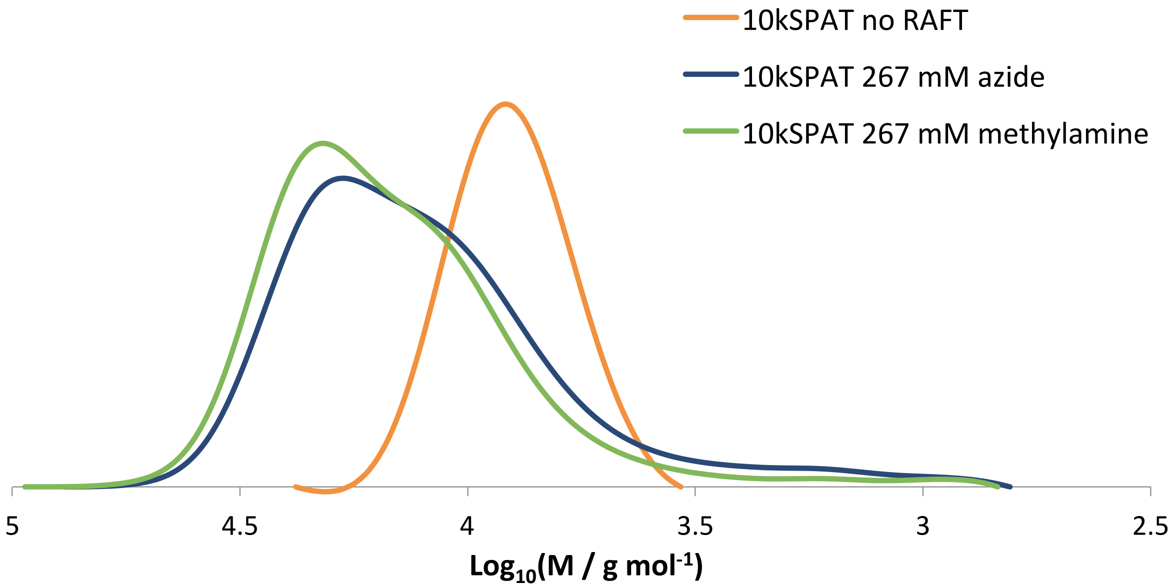

Figure S10. Disulphide coupling from thiol-terminated polymers generated after 48 hours of 267 mM sodium azide or methylamine attack on SPAT CTA.

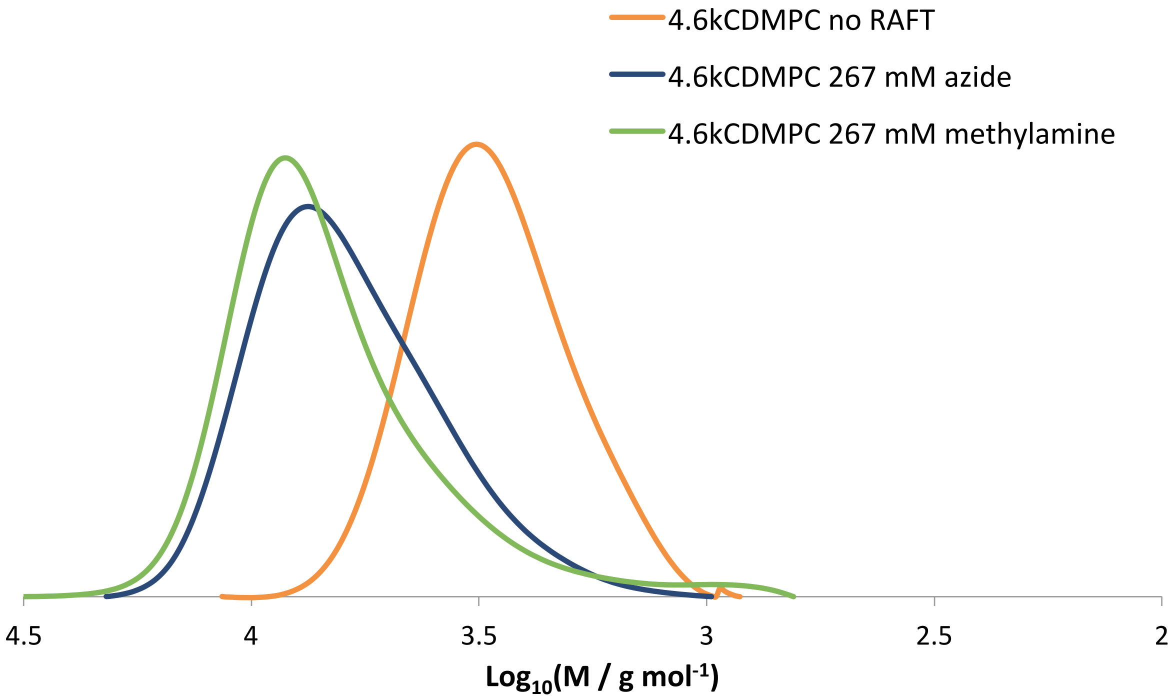

Figure S11. Disulphide coupling from thiol-terminated polymers generated after 48 hours of 267 mM sodium azide or methylamine attack on CDMPC CTA.

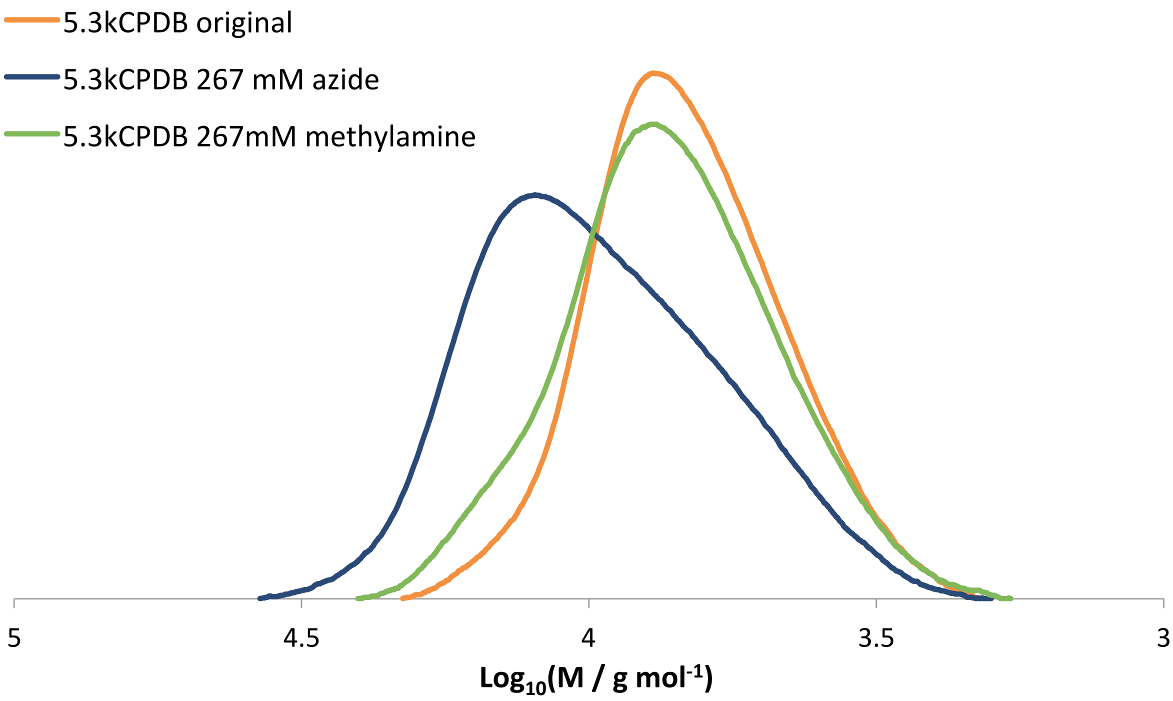

Figure S12. Disulphide coupling from thiol terminated polymers generated after 48 hours of 267 mM sodium azide or methylamine attack on CPDB CTA.

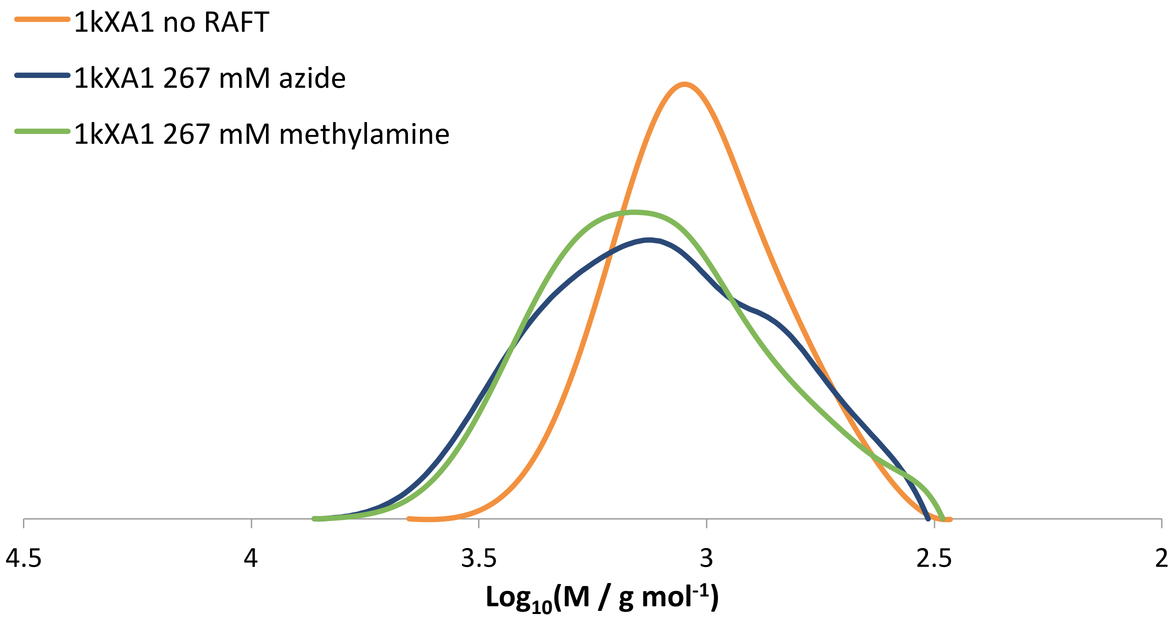

Figure S13. Disulphide coupling from thiol-terminated polymers generated after 48 hours of 267 mM sodium azide or methylamine attack on XA1 CTA.

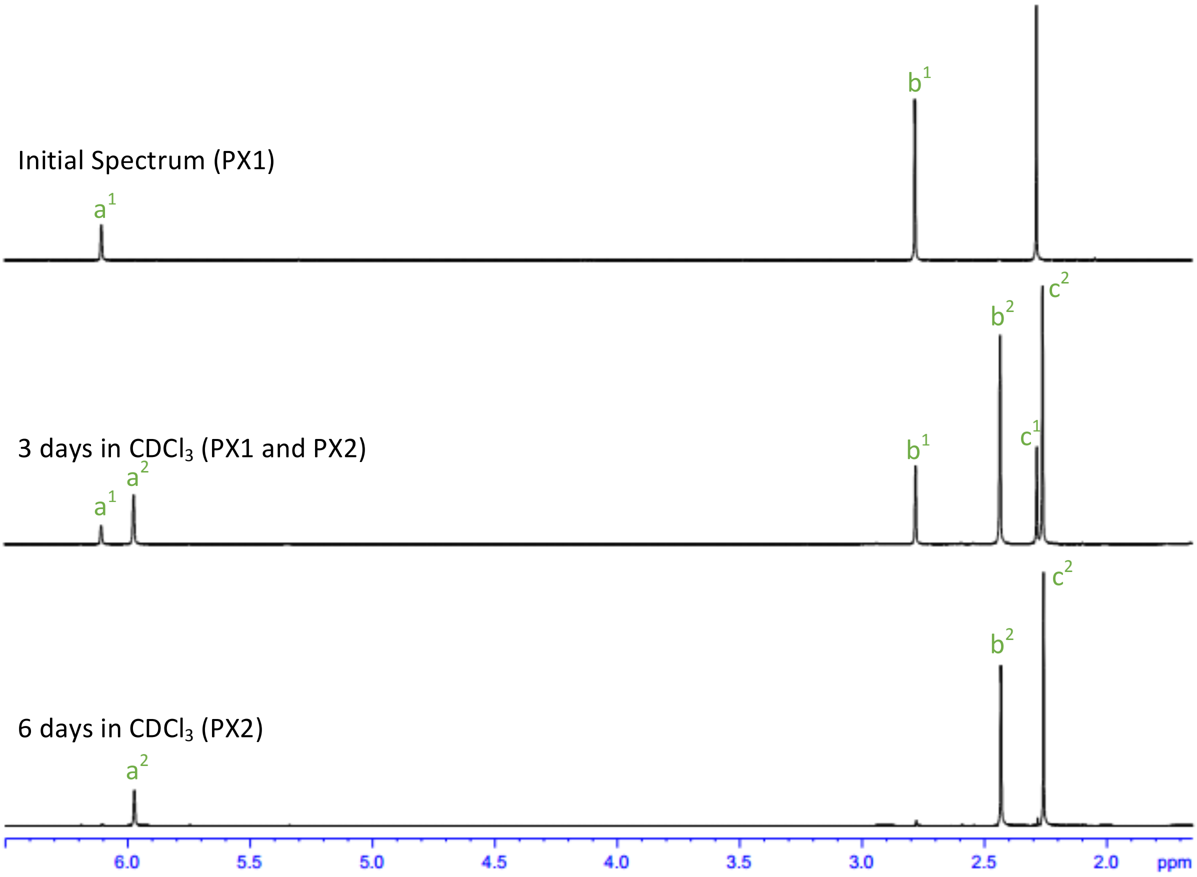

Figure S14. ^{1}H-NMR ($CDCl_3$) over time of precipitated solid from sodium azide reaction with **4.6kCDMPC**.

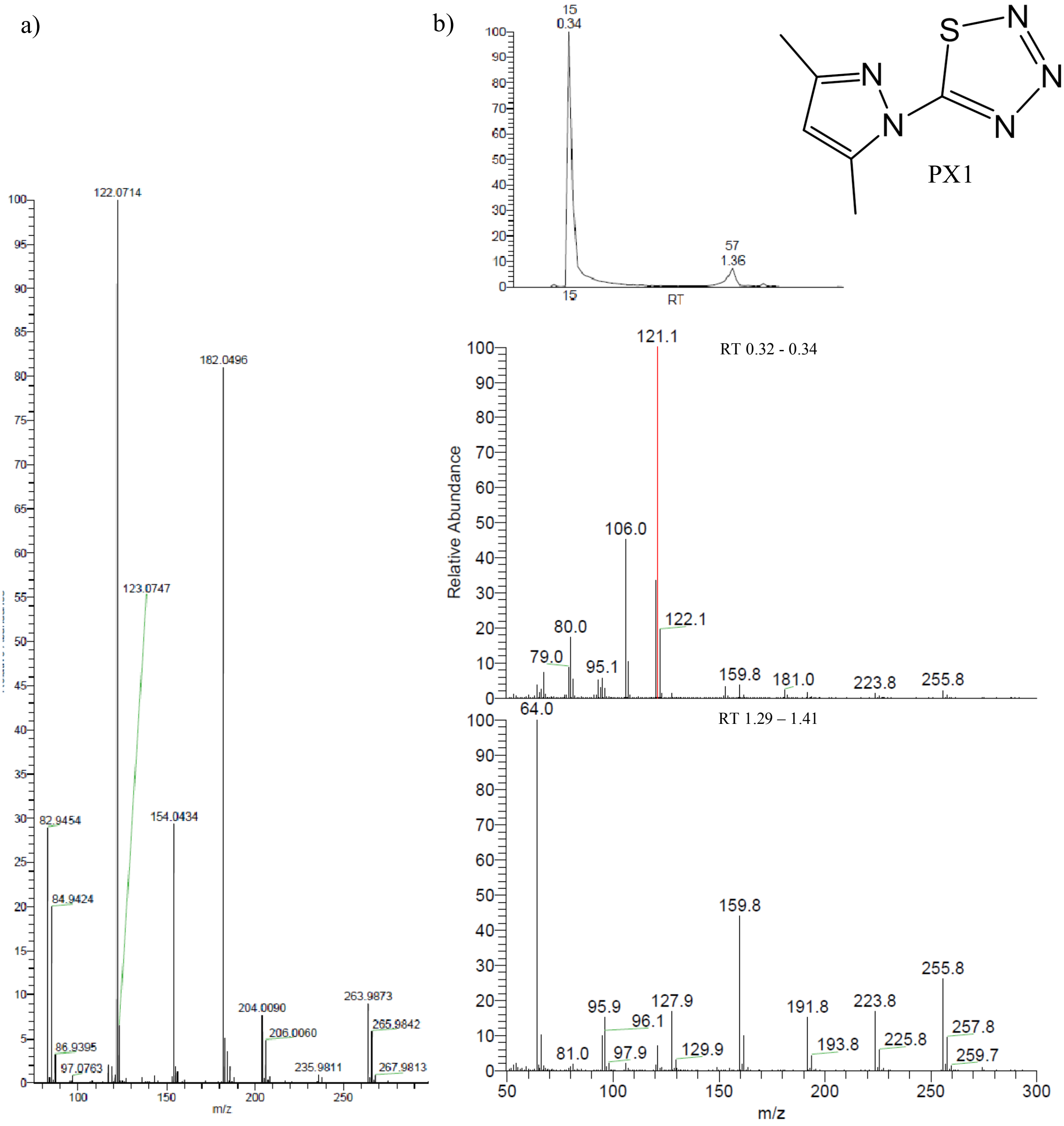

Figure S15. Mass spectra for **PX1** as analysed by a) APCI-MS (calculated for $C_6H_7N_5S$ +1H$^+$ 182.0500, found 182.0496) and b) EI-MS (calculated for $C_6H_7N_5S$ 181.0422, found 181.0; calculated for S_8 255.7767, found 255.8).

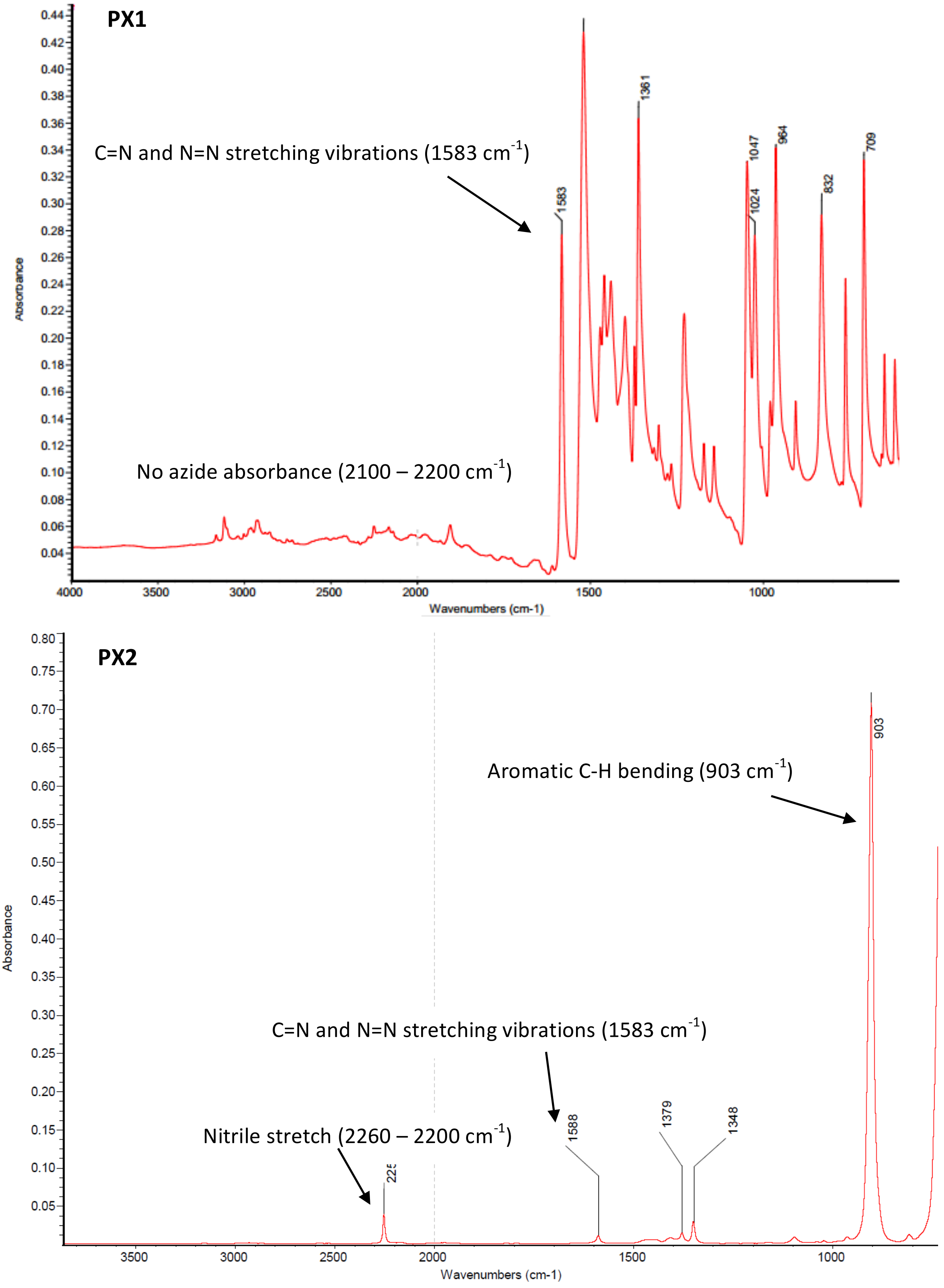

Figure S16. FTIR spectra for **PX1** (solid state) and **PX2** (in $CDCl_3$ with the $CDCl_3$ signal subtracted).

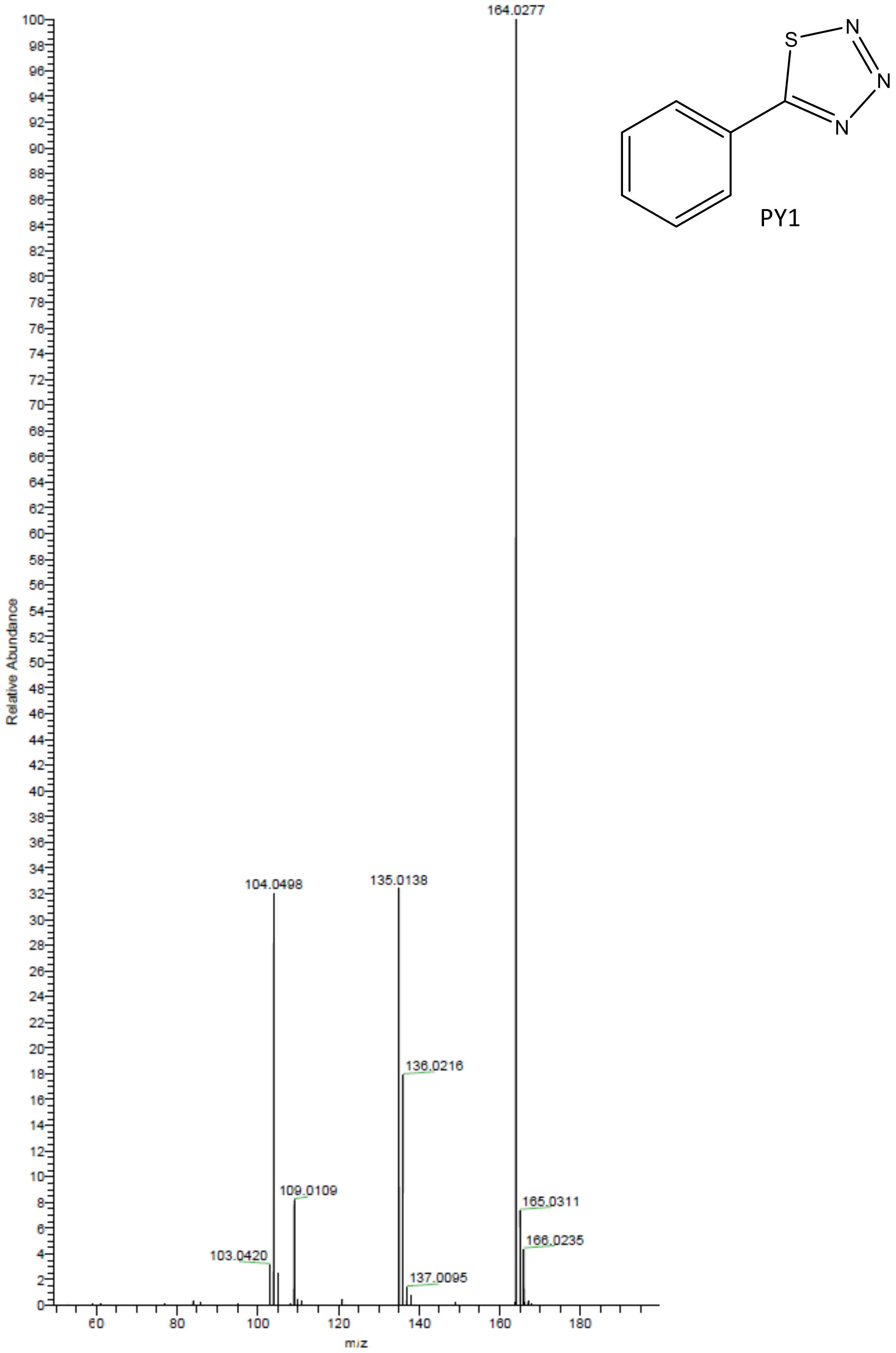

Figure S17. Mass spectra for solid precipitate formed after reaction of sodium azide and **5.3kCPDB** (PY1) as analysed by APCI-MS (calculated for $C_7H_5N_3S$ $+1H^+$ 164.0277, found 164.0277)

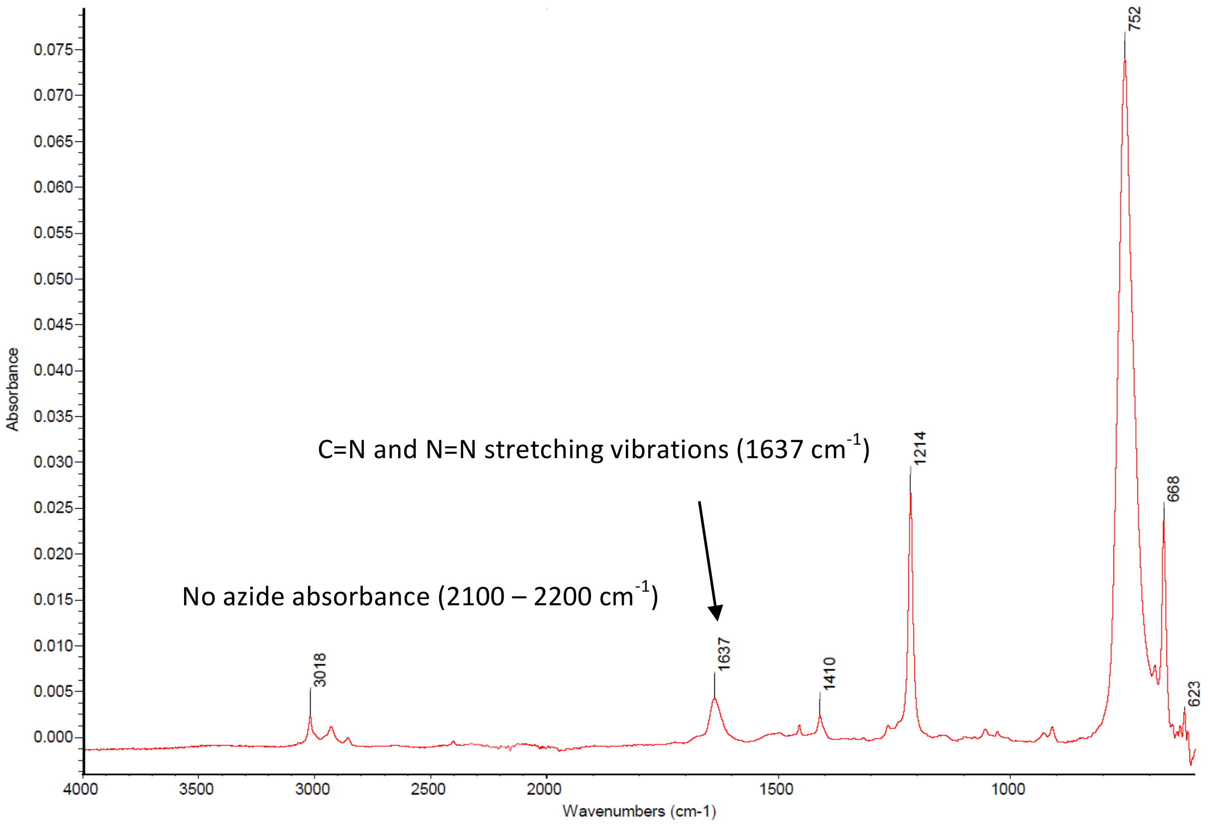

Figure S18. Infrared spectroscopy spectrum for **PY1** (in $CHCl_3$) with peaks at 3016cm^{-1} and 752cm^{-1} attributed to the chloroform solvent.