SUPPORTING INFORMATION

Ultra-fast aqueous polymerisation of acrylamides by high power visible light direct photoactivation RAFT polymerisation

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Figure S1. a) Photograph of 402 nm photoreactor with glass tube loaded. b) Photograph of 451 nm photoreactor with glass tube loaded. c) Comparison of NMR tube in glass jacket (left) with glass tube (right) as vessels for photo reactions. d) Photograph inside the 451 nm photoreactor with LEDs turned on.



Figure S2. GPC plots demonstrating living nature of DP-RAFT polymerisations of AM ($[AM]_0 = 2 M$, [AM]:[DMAT] = 140:1, H₂O/dioxane 80:20) under different wavelengths and intensities of visible light. Chain extension data from all polymerisations is also overlayed in the bottom left, demonstrating nearly identical results at all intensities and wavelengths.



Figure S3. Linear molecular weight growth with conversion for DP-RAFT polymerisations of AM ($[AM]_0 = 2 \text{ M}, [AM]:[DMAT] = 140:1, H_2O/dioxane 80:20$) under different wavelengths and intensities of visible light as measured by ¹H NMR spectroscopy. This was carried out by integrating polymer CH₂ peaks (1.2 – 1.8 ppm, 2H per unit) against CH₃ groups on DMAT (0.9 – 1.1 ppm, 12H).

Table S1. Conversion and GPC data for DP-RAFT polymerisations of AM under temperature controlled (30°C) and non-temperature controlled conditions ($[AM]_0 = 2M$, [AM]:[DMAT] = 140:1, D₂O/dioxane 80:20).

Sample	Time (min)	Conversion (%)	M _{n,GPC} (g mol⁻¹)	Ð
104 W (402 nm, glass tube no temp)	20	88	6,440	1.19
104 W (402 nm, NMR tube no temp)	53	90	6,890	1.21
208 W (402 nm, 30°C)	100	87	7,780	1.23
108 W (402 nm, 30°C)	150	87	6,550	1.22
26 W (402 nm, 30°C)	360	87	6,090	1.21

Table S2. Experimental parameters and results of control experiments conducted.

Sample	[DMA]:[AM]: [DMAT]	Light wavelength (nm)	Light power (W)	Time (min)	Conversion (%)	M _{n,GPC} (g mol ⁻¹)
1	140:0:1	402	208	8	99	11,800
2	140:0:0	402	208	10	13	Broad*
3	0:140:1	402	208	11	87	6,250
4	0:140:0	402	208	10	12	787,000
5	140:0:0	451	26	240	48	547,000
6	0:140:1	451	26	240	89	6,300
7	0:140:0	451	26	240	50	563,000
8	140:0:1	Dark, heated 70°C	-	30	0	-
9	0:140:1	Dark, heated 70°C	-	30	0	-

*Did not elute properly through column.

Included is polymerisations conducted without CTA (DMAT) along with those conducted with a CTA (DMAT) for comparison. Experiments conducted in the dark, heated to 70°C are also shown.

 Table S3. Ultra-high molecular weight DP-RAFT polymerisations of AM and DMA to 7,000

and 28,000 DP at different wavelengths and intensities of visible irradiation.

Sample name*	Time (h)	Conversion (%)	M _{n,theory} (g mol ⁻¹)	M _{n,GPC} (g mol ⁻¹)	Ð
28kAM(108 W 402 nm)	2.5	85	1,690,000	1,647,000	1.36
7kAM(108 W 402 nm)	2.2	88	438,000	364,000	1.44
7kAM(208 W 402 nm)	0.67	79	391,000	324,000	1.43
7kAM(26 W 402 nm)	5.6	78	390,500	351,000	1.36
7kAM(26 W 451 nm)	18.2	73	363,000	358,000	1.36
28kDMA(108 W 402 nm)	2	74	2,054,000	1,765,000	1.43
7kDMA(26 W 451 nm)	13	85	712,280	670,000	1.32

*Samples were named according to XM(Y Z) where X is the target DP, M is the monomer abbreviation (AM or DMA), Y is the irradiation power and Z is the irradiation wavelength.



Figure S4. Close agreement in elution time detected by both RI and UV (305 nm) detectors for a) 7kAM(26 W 451 nm) and b) 28kAM(26 W 451 nm) suggesting retention of trithiocarbonate end groups. c) Plot of UV absorbance (250 – 400 nm) measured by the photodiode array detector at an elution time of 14.4 minutes for 7kAM(26 W 451 nm) showing expected spectrum for a trithiocarbonate group.