Electronic Supplementary Material (ESI) for Polymer Chemistry. This journal is © The Royal Society of Chemistry 2022

Supporting information (SI) for:

Autonomous polymer synthesis delivered by multi-objective

closed-loop optimisation

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Experimental

Automated Platform

The automated platform consisted of: a Jasco PU-1580 HPLC pump; a custom-built flow reactor – a stainless steel tubular reactor (0.7 mm I.D, 2 mL), wrapped around a block heated by a Eurotherm 3210 controller fitted with two Elmatic Max K cartridges, with a 100 psi backpressure regulator; a benchtop NMR instrument and a custom-built GPC instrument.



Online Gel permeation chromatography (GPC)

The custom-built gel permeation chromatography (GPC) setup was constructed using a Jasco PU-980 HPLC pump (flow rate: 2 ml min⁻¹), GPC columns (Agilent Rapide M plus guard) and a Knauer 2301 refractive index (RI) detector, all controlled by a homemade MatLab program, as is shown in Figure S1. THF eluent was used with triethylamine (1 % w/v). The program records the time of injection from the triggering of the switching valve, and the subsequent RI trace. Molecular weights can then be calculated from calibration to a series of near-monodisperse standards (PMMA – M_p: 885–2,200,000 g mol⁻¹). The injection volume is approximately 3 μ I.



Figure S1. Schematic of the online analysis used with the automated platform reported in this work.



Figure S2. A representation of the switching valve in either the a) loading state or b) injection state. When acquiring a sample for GPC analysis, the valve will switch to the loading state for a very short period of time (100 ms).



Figure S3. Example elution of PMMA standards (M_p :800 - 2,200,000 g mol⁻¹) from online GPC setup, used for calibration for molecular weight measurements.



Figure S4. Example calibration curve from elution of PMMA standards (from Figure S3).

Offline GPC

Offline GPC measurements were conducted with an Agilent 11260 Infinity system, fitted with two 5 μ m Mixed-C columns (with guard column), an RI detector and a UV-Vis detector operating at 309 nm. DMF containing 1 % w/v LiBr was used as the eluent system at 1 ml min⁻¹, with the column oven and RI detector at 60 °C. A series of near-monodisperse PMMA standards were used (M_p: 800–2,200,000 g mol⁻¹) for calibration.

NMR

NMR spectra were recorded using a Magritek Spinsolve 60 Ultra. They were collected using a presaturation solvent suppression routine (1s saturation pulse at 3.3 ppm of -65 dB, 7 μ s excitation pulse, spectral width of 5 kHz (32,768 points), acquisition time of 6.4 s, repetition time of 10 s and number of scans = 2) All chemical shifts are reported in ppm (δ). Conversion for monomers is calculated as per **Equation S1-3**, and for n-butyl acrylate is calculated as per .

$$\alpha = 1 - \frac{[M]}{[M] + [P]} = 1 - \frac{6x}{1.5x + y}$$

Equation S1. Conversion for the polymerisation of tert-butyl acrylamide (^tBuAm), where x is the vinyl peak between 5.8 and 6.4 ppm (2 protons) and y is the overlapping monomer and polymer region between 2.3 and 0.0 ppm (9 monomer protons, 12 polymer protons)

$$\alpha = 1 - \frac{[M]}{[M] + [P]} = 1 - \frac{10x}{3(x+y)}$$

Equation S2. Conversion for the polymerisation of n-butyl acrylate (BuA), where x is the vinyl peak between 5.35 and 6.6 ppm (3 protons) and y is the overlapping monomer and polymer region between 2.75 and 0.0 ppm (7 monomer protons, 10 polymer protons)

$$\alpha = 1 - \frac{[M]}{[M] + [P]} = 1 - \frac{5x}{2(x+y)}$$

Equation S3. Conversion for the polymerisation of methyl methacylate (MMA), where x is the vinyl peak between 4.9 and 6.6 ppm (2 protons) and y is the overlapping monomer and polymer region between 2.17 and 0.0 ppm (3 monomer protons, 5 polymer protons)

Initial testing

Initial testing of the simultaneous dispersity and conversion measurements with a constant stream of partially converted (44 %) poly(tert-butyl acrylamide) gave standard deviations of 0.014 and 0.003 respectively over 22 measurements.

Time (s)	Number average molecular weight, Mn (g mol ⁻¹)	Peak molecular weight, M _P (g mol ⁻¹)	Dispersity	Conversion
0	13110.31	17043.18	1.2084	0.4358
450	12731.20	15941.89	1.1838	0.4423
900	13036.58	16208.87	1.1949	0.4459
1350	13213.38	15692.88	1.2086	0.4424
1800	13322.89	16981.34	1.2084	0.4422
2250	11859.08	16124.58	1.2372	0.4403
2700	13270.64	15564.60	1.1717	0.4418
3150	13302.00	17214.71	1.2111	0.4403
3600	12990.66	14723.64	1.1960	0.4461
4050	12625.78	15642.52	1.1912	0.4441
4500	12754.27	15470.60	1.1912	0.4374
4950	13188.80	15242.68	1.2094	0.4459
5400	12406.18	15729.36	1.2037	0.4403
5850	12332.71	14460.81	1.1998	0.4416
6300	13013.40	15547.96	1.2089	0.4427
6750	12527.21	15369.10	1.2181	0.4383
7200	13088.27	15572.92	1.1827	0.4445
7650	13168.10	16336.31	1.1963	0.4380
8100	13254.87	17103.77	1.2060	0.4420
8550	12904.10	15926.19	1.1908	0.4397
9000	13213.23	15563.20	1.2056	0.4424
9450	12637.80	15632.77	1.1865	0.4460
		Average	1.2005	0.4418
		Standard deviation	0.0140	0.0029

 Table S1. Initial testing for consistency of measurement of platform

Materials

2,2-azobis(2-methylpropionitrile) (AIBN, 98 %), 1,1-Azobis(cyclohexanecarbonitrile) (ACHN, 98 %), n-butyl acrylate (BuA, \geq 99%, stabilised for synthesis), (Sigma-Aldrich (UK)); methyl methacrylate (MMA, 99 %, Acros Organics); 3-((((1-carboxyethyl)thio)carbonothioyl)thio) propanoic acid (TTC-1, \geq 90 %) and 4-((((2-carboxyethyl)thio)carbonothioyl)thio)-4-cyanopentanoic acid (TTC-2, \geq 95 %), 2-(Butylthiocarbonothioylthio)propanoic acid (TTC-4, \geq 95 %), 2-cyanobutan-2-yl 4-chloro-3,5-dimethyl-1H-pyrazole-1-carbodithioate (Py-DTC-1, \geq 95 %) (Boron Molecular (Raleigh, USA)); and tert-butylacrylamide (^tBuAm, 97 %, Alfa-Aesar (UK)) were used as supplied. 2-(((methylthio) carbonothioyl)thio)phenyl acetic acid (TTC-3, ~90%) was donated by Thomas Howell, synthesised using a previously reported literature method.¹ Inhibitor was removed from BuA by passing through silica for the "inhibitor removed" experiment.

Automated experiments

tert-Butylacrylamide (100 g, 200 eq), RAFT agent (TTC-1, TTC-2, TTC-3, TTC-4 and Py-DTC-1) (1 eq) and AIBN (0.065 g, 0.1 eq) were dissolved in methanol (300 mL) to give a 30 % w/w solution, sealed and connected to the automated platform.

n-Butyl acrylate (100 g, 200 eq), TTC-1 (~1 g, 1 eq) and initiator (AIBN or ACHN) (0.1 eq) were dissolved in dioxane (228 mL) to give a 30 % w/w solution, sealed and connected to the automated platform.

Methyl methacrylate (100 g, 200 eq), TTC-2 (2.01 g, 1 eq) and ACHN (0.244 g, 0.2 eq) were dissolved in dioxane (231 mL) to give a 30 % w/w solution, sealed and connected to the automated platform.

¹ D. J. Keddie, G. Moad, E. Rizzardo and S. H. Thang, *Macromolecules*, 2012, **45**, 5321–5342.

Additional Data

Initiator Decay



Figure S5. Relative concentration of AIBN over time for the temperatures used in the automated screen



Figure S6. Radical concentration over time for the range of temperatures used in this work for (a) AIBN and (b) ACHN

Automated Screen



Figure S7. GPC traces for the experiments performed in the automated full-factorial DoE screen of the synthesis of $P(^{t}BuAm)_{200}$ using TTC-1 as the RAFT agent.



Figure S8. NMR spectra for the programmed screen of the RAFT polymerisation of ^tBuAm, using TTC-1 as the CTA. Experiment number increases from bottom to top.

Experiment number	Integral (6.4 – 5.8)	Integral (2.3 – 0.0)	Conversion (%)
1	154.36	704.90	1.10
2	153.33	709.08	2.03
3	154.54	705.83	1.11
4	153.57	708.26	1.83
5	155.46	702.73	0.34
6	153.95	708.66	1.69
7	154.49	704.81	1.03
8	153.85	707.74	1.64
9	153.78	706.99	1.60
10	138.19	731.11	11.64
11	155.70	704.63	0.43
12	97.28	791.61	37.74
13	58.47	844.37	62.36
14	41.79	859.22	72.80
15	31.75	868.41	79.21
16	79.29	829.34	49.83
17	43.44	853.15	71.62
18	33.19	866.50	78.27
19	29.22	870.54	80.82
20	25.94	876.66	83.00
21	53.41	847.01	65.43
22	38.01	860.35	75.14
23	36.61	864.68	76.11
24	38.84	861.55	74.67
25	36.50	864.28	76.17

Table S2. Integrals and conversion obtained for the programmed screen of the RAFT polymerisation of ^tBuAm, using TTC-1 as the CTA.

TSEMO optimisations for the RAFT polymerisation of ^tBuAm (Limits = 4-20 mins; 80-116 °C)



Figure S9. GPC traces for each of the experiments performed by the automated platform for the RAFT polymerisation of ^tBuAm using (a) TTC-1, (b) TTC-2, (c) TTC-3, (d) TTC-4 and (e) Py-DTC-1 as the RAFT agent. Colour becomes lighter as experiment number increases.

Offline GPC

Following these experiments, a steady state sample was taken for comparison of online and offline GPC. The conditions used were from the TTC-2 experiment – at 94 °C and 20 mins residence time, which gave a D of 1.24. Five repeats were run for the offline GPC, which gave a slightly higher average D of 1.28. The automated processing of chromatograms loses a little of the low intensity data from either side of the peak which is the cause of the slight increase in D. However, since the results are internally consistent and therefore comparable, there was no need to improve the processing.



Figure S10. Offline GPCs for a steady state RAFT polymerisation of polymerisation of ^tBuAm, using TTC-2 as the CTA, at a temperature of 94 °C and a residence time of 20 mins.



Figure S11. NMR spectra for the 28 experiments completed for the RAFT polymerisation of ^tBuAm in the optimisation using TTC-1 as the CTA. Experiment number increases from bottom to top

Experiment number	Integral (6.4 – 5.8)	Integral (2.3 – 0.0)	Conversion (%)
1	132.16	765.68	17.77
2	140.48	693.22	6.73
3	90.93	763.24	39.40
4	139.32	718.41	9.91
5	40.94	826.21	72.18
6	39.39	828.94	73.32
7	26.74	844.61	82.03
8	28.09	839.90	80.89
9	37.89	833.41	74.55
10	40.28	829.69	72.98
11	26.51	840.76	81.96
12	34.26	834.99	76.83
13	40.27	830.63	72.89
14	26.74	840.86	81.68
15	26.68	842.86	81.79
16	28.81	840.83	80.26
17	28.29	844.76	81.11
18	31.84	836.40	78.54
19	36.76	834.42	75.36
20	36.41	833.81	75.40
21	35.99	836.26	75.02
22	36.95	830.49	74.88
23	34.40	836.81	77.00
24	30.76	839.32	79.54
25	66.63	816.66	56.44
26	29.94	842.09	79.80
27	55.80	824.78	63.39
28	36.59	833.14	75.08

Table S3. Integrals and conversion obtained for the 28 experiments completed for the RAFT polymerisation of ${}^{t}BuAm$, using TTC-1 as the CTA



Figure S12. NMR spectra for the 36 experiments completed for the RAFT polymerisation of ^tBuAm, using TTC-2 as the CTA. Experiment number increases from bottom to top

Experiment number	Integral (6.4 – 5.8)	Integral (2.3 – 0.0)	Conversion (%)
1	140.52	661.63	3.93
2	141.53	670.90	4.66
3	142.02	673.05	4.43
4	74.79	769.36	49.47
5	83.68	759.97	43.29
6	87.95	755.01	40.67
7	100.11	756.72	34.18
8	38.40	814.00	73.97
9	33.54	821.31	77.43
10	66.50	799.58	55.64
11	64.83	796.20	56.70
12	95.15	777.97	39.22
13	74.91	779.98	50.17
14	51.68	803.57	64.96
15	36.40	819.04	75.28
16	36.48	818.31	74.16
17	40.49	812.84	72.20
18	41.30	810.30	71.61
19	34.24	818.79	76.93
20	30.42	822.32	77.30
21	31.35	819.06	78.44
22	30.86	822.71	78.33
23	31.32	823.75	78.60
24	28.15	826.18	80.56
25	32.03	820.62	79.12
26	30.78	824.42	80.48
27	28.38	826.60	80.10
28	35.00	818.09	75.74
29	49.55	802.23	66.72
30	33.10	818.80	78.42
31	30.58	820.51	78.78
32	28.51	822.78	80.09
33	33.01	816.33	77.56
34	33.05	818.56	77.11
35	29.71	822.96	78.74
36	45.73	798.66	68.61

Table S4. Integrals and conversion obtained for the 36 experiments completed for the RAFT polymerisation of ^tBuAm, using TTC-2 as the CTA.



Figure S13. NMR spectra for the 25 experiments completed for the RAFT polymerisation of ^tBuAm, using TTC-3 as the CTA. Experiment number increases from bottom to top

Experiment number	Integral (6.4 – 5.8)	Integral (2.3 – 0.0)	Conversion (%)
1	147.19	693.31	3.86
2	148.60	695.31	3.17
3	146.59	695.50	3.31
4	145.01	695.91	4.93
5	146.04	696.25	4.54
6	145.28	695.64	4.88
7	146.33	694.18	4.82
8	123.55	732.46	20.47
9	96.70	769.61	37.00
10	143.48	716.90	8.13
11	96.25	772.92	37.46
12	97.48	768.65	36.32
13	115.87	743.80	24.4
14	93.64	779.87	38.94
15	102.48	763.41	33.4
16	98.00	769.48	36.49
17	98.33	767.17	35.81
18	99.86	766.33	35.05
19	96.60	766.27	37.10
20	106.51	756.19	30.34
21	107.37	754.23	29.91
22	92.14	777.27	39.85
23	91.37	779.56	40.28
24	136.84	730.57	10.55
25	101.46	766.39	33.69

Table S5. Integrals and conversion obtained for the 25 experiments completed for the RAFT polymerisation of ^tBuAm, using TTC-3 as the CTA.



Figure S14. NMR spectra for the 23 experiments completed for the RAFT polymerisation of ^tBuAm, using TTC-4 as the CTA. Experiment number increases from bottom to top

Experiment number	Integral (6.4 – 5.8)	Integral (2.3 – 0.0)	Conversion (%)
1	133.03	624.73	3.19
2	48.50	744.39	64.40
3	39.55	756.66	71.02
4	71.23	719.93	48.38
5	28.76	767.14	78.88
6	32.65	760.63	75.86
7	22.63	771.34	83.06
8	21.89	772.96	83.86
9	31.84	762.25	76.43
10	34.16	760.22	74.75
11	19.58	772.23	85.35
12	23.68	767.65	82.15
13	21.79	771.15	83.72
14	19.74	774.30	85.23
15	25.76	768.55	80.84
16	28.64	765.78	78.55
17	28.40	766.35	78.87
18	26.33	767.72	80.60
19	27.03	767.19	79.95
20	23.76	772.35	80.57
21	37.00	759.28	72.79
22	23.13	772.03	82.73
23	23.11	770.24	82.85

Table S6. Integrals and conversion obtained for the 23 experiments completed for the RAFT polymerisation of ^tBuAm, using TTC-4 as the CTA.



Figure S15. NMR spectra for the 25 experiments completed for the RAFT polymerisation of ^tBuAm, using Py-DTC-1 as the CTA. Experiment number increases from bottom to top

Experiment number	Integral (6.4 – 5.8)	Integral (2.3 – 0.0)	Conversion (%)
1	130.01	613.06	3.48
2	131.73	611.46	2.32
3	111.79	646.24	17.6
4	130.30	617.40	3.82
5	48.18	733.16	64.02
6	58.21	722.68	56.89
7	29.13	750.61	78.22
8	21.29	758.18	83.82
9	42.70	734.49	67.91
10	34.01	746.25	74.42
11	23.95	755.10	81.83
12	25.38	757.50	80.84
13	26.60	754.98	79.89
14	26.76	752.08	79.73
15	24.24	756.12	81.65
16	23.46	754.25	82.16
17	46.61	733.56	65.21
18	36.02	741.75	72.84
19	30.72	749.39	76.82
20	30.38	749.21	76.98
21	29.28	748.36	77.81
22	24.53	753.95	81.39
23	22.14	753.91	83.11
24	23.54	756.03	82.17
25	22.17	756.76	83.14

Table S7. Integrals and conversion obtained for the 25 experiments completed for the RAFT polymerisation of ^tBuAm, using Py-DTC-1 as the CTA.

Figure S16. The number average molecular weight vs conversion for the RAFT polymerisation of tBuAm, using (a) TTC-1, (b) TTC-2, (c) TTC-3, (d) TTC-4 and (e) Py-DTC-1 as the RAFT agent.

TSEMO optimisation for the RAFT polymerisation of ^tBuAm using TTC-3 as the RAFT agent (Limits = 3-30 mins; 80-116 °C)

An additional optimisation was performed for the RAFT polymerisation of ^tBuAm using TTC-4 as the RAFT agent, with wider search limits and an adjustment to the TSEMO algorithm where the "batch size" of the TSEMO algorithm was 1 instead of 4. Previous work has shown that a batch of 4 experiments before each iteration of the TSEMO can increase the speed of experiments, to reduce the "dead-time" while awaiting experimental results from analyses such as GPC which have an associated lag-time. However, in this application, a degree of clustering of conditions was noted within each batch – meaning a greater efficiency in exploration could be achieved using a batch size of 1.

Figure S17. Flow reactor conditions for the optimisation for the RAFT polymerisation of ^tBuAm and TTC-4 as the RAFT agent using wider condition limits and a smaller batch size in the TSEMO algorithm

Figure S18. GPC traces for the 23 experiments performed by the automated platform for the RAFT polymerisation of ^tBuAm and TTC-4 as the RAFT agent using wider condition limits and a smaller batch size in the TSEMO algorithm. Colour becomes lighter as experiment number increases.

Figure S19. The number average molecular weight vs conversion for the RAFT polymerisation of ^tBuAm, using TTC-4 as the RAFT agent using wider condition limits and a smaller batch size in the TSEMO algorithm.

Figure S20. NMR spectra for the 23 experiments performed by the automated platform for the RAFT polymerisation of ^tBuAm and TTC-4 as the RAFT agent using wider condition limits and a smaller batch size in the TSEMO algorithm. Experiment number increases from bottom to top

Experiment number	Integral (6.4 – 5.8)	Integral (2.3 – 0.0)	Conversion (%)
1	244.27	1161.70	4.09
2	70.26	1389.14	71.79
3	52.70	1421.39	78.93
4	125.06	1352.42	51.28
5	44.32	1423.05	82.15
6	47.43	1429.92	81.04
7	39.21	1430.36	84.20
8	37.62	1435.76	84.87
9	58.81	1415.39	76.53
10	61.20	1411.91	75.58
11	35.52	1438.18	85.71
12	56.83	1423.03	77.39
13	93.12	1392.42	63.53
14	56.75	1417.73	77.34
15	103.44	1361.21	59.07
16	98.56	1372.54	61.11
17	43.78	1424.93	82.38
18	46.03	1424.81	81.51
19	51.21	1419.15	79.46
20	57.47	1416.41	77.05
21	191.12	1242.11	24.99
22	72.41	1401.80	71.24
23	52.92	1419.47	78.82

Table S8. Integrals and conversion obtained for the 23 experiments performed by the automated platform for the RAFT polymerisation of ^tBuAm and TTC-4 as the RAFT agent using wider condition limits and a smaller batch size in the TSEMO algorithm.

TSEMO optimisation for the RAFT polymerisation of n-butyl acrylate

Figure S21. Multi-objective optimisations (TSEMO algorithm) for the RAFT polymerisation of n-butyl acrylate, and TTC-1 as the RAFT agent ([monomer]:[CTA]:[initiator] 200:1:0.1). [Condition limits: 3-30 mins, 80-120 °C] (a) and (b) use AIBN as the initiator, with (a) using the monomer as supplied and (b) with the inhibitor removed. (c) uses ACHN as the initiator.

To investigate the influence of radical concentration at higher temperatures upon dispersity, the same system used in experiment (a) was repeated, with a change to the higher temperature initiator to 1,1-Azobis(cyclohexanecarbonitrile) (ACHN). This results in a lower radical flux at equivalent temperatures. The results show that the high dispersities are largely driven by the polymerisation kinetics themselves, increased dispersities across the range of conditions.

Figure S22. Flow reactor conditions for the optimisations for the RAFT polymerisation of n-butyl acrylate (a) as supplied and (b) with inhibitor removed using TTC-1 as the RAFT agent and AIBN as the initiator. (c) uses the same system as (a) but with ACHN as the initiator.

Figure S23. GPC traces for each of the experiments performed by the automated platform for the polymerisation of n-butyl acrylate (a) as supplied and (b) with inhibitor removed using TTC-1 as the RAFT agent and AIBN as the initiator. (c) uses the same system as (a) but with ACHN as the initiator. Colour becomes lighter as experiment number increases.

Figure S24. NMR spectra for the 19 experiments completed for the RAFT polymerisation of *n*-BuA as supplied, using TTC-1 as the CTA and AIBN as the initiator. Experiment number increases from bottom to top

Experiment number	Integral (6.6 – 5.35)	Integral (2.75 – 0.0)	Conversion (%)
1	438.77	1073.16	3.27
2	170.21	1379.27	63.38
3	168.28	1390.15	64.01
4	284.56	1248.81	38.14
5	145.94	1420.82	68.95
6	144.42	1419.10	69.21
7	115.47	1455.47	75.50
8	106.07	1464.54	77.49
9	161.11	1407.95	65.77
10	153.53	1404.44	67.15
11	97.98	1472.82	79.21
12	133.24	1437.80	71.73
13	117.76	1451.12	74.98
14	204.01	1347.22	56.16
15	162.43	1401.12	65.37
16	134.53	1428.34	71.31
17	150.50	1417.79	68.01
18	176.51	1389.13	62.42
19	204.57	1355.21	56.28

Table S9. Integrals and conversion obtained for the 19 experiments completed for the RAFT polymerisation of *n*-BuA as supplied, using TTC-1 as the CTA and AIBN as the initiator.

Figure S25. NMR spectra for the 22 experiments completed for the RAFT polymerisation of *n*-BuA after inhibitor removal, using TTC-1 as the CTA and AIBN as the initiator. Experiment number increases from bottom to top

Experiment number	Integral (6.6 – 5.35)	Integral (2.75 – 0.0)	Conversion (%)
1	232.79	581.41	4.69
2	73.03	772.83	71.22
3	72.91	780.79	71.53
4	135.64	711.18	46.61
5	64.34	791.78	74.95
6	66.08	793.33	74.37
7	56.14	805.84	78.29
8	51.74	810.47	80.00
9	79.48	778.60	69.12
10	73.29	781.64	71.43
11	65.02	795.47	74.81
12	119.64	728.99	53.01
13	64.62	794.92	74.94
14	61.97	799.45	76.02
15	55.01	805.00	78.68
16	93.62	761.98	63.53
17	57.73	803.11	77.65
18	104.08	745.95	59.19
19	72.90	788.24	71.78
20	58.40	802.11	77.38
21	76.97	779.83	70.06
22	51.89	809.82	79.93

Table S10. Integrals and conversion obtained for the 22 experiments completed for the RAFT polymerisation of *n*-BuA after inhibitor removal, using TTC-1 as the CTA and AIBN as the initiator.

Figure S26. NMR spectra for the 19 experiments completed for the RAFT polymerisation of *n*-BuA as supplied, using TTC-1 as the CTA and ACHN as the initiator. Experiment number increases from bottom to top

Experiment number	Integral (6.6 – 5.35)	Integral (2.75 – 0.0)	Conversion (%)
1	418.35	1059.63	5.65
2	335.53	1154.15	24.92
3	329.99	1154.59	25.91
4	404.13	1060.61	8.03
5	283.86	1222.14	37.17
6	264.44	1245.18	41.61
7	178.77	1355.79	61.17
8	136.23	1411.68	70.66
9	226.39	1298.20	50.50
10	152.93	1393.58	67.04
11	203.02	1328.48	55.81
12	98.54	1453.84	78.84
13	90.29	1466.66	80.67
14	106.44	1448.98	77.19
15	136.06	1411.09	70.69
16	166.32	1374.95	64.03
17	202.53	1328.38	55.90
18	131.58	1414.73	71.64
19	120.71	1429.89	74.05

Table S11. Integrals and conversion obtained for the 19 experiments completed for the RAFTpolymerisation of n-BuA as supplied, using TTC-1 as the CTA and ACHN as the initiator.

TSEMO optimisation for the RAFT polymerisation of methyl methacrylate

Figure S27. Flow reactor conditions for the optimisation for the RAFT polymerisation methyl methacrylate. A large pressure drop can be observed around 40 hours, indicating that the reactor is not behaving ideally and therefore data obtained after this point is discarded as invalid. The data presented in the manuscript relates only to the data acquired before this pressure drop. Furthermore, there are flatlines present in the flow rate and reactor temperature between 10 hours and 17 hours. These relate to an error in the NMR software overnight, which was rectified upon discovery in the morning, and the experiment was able to proceed.

Figure S28. GPC traces for the 17 experiments performed by the automated platform for the polymerisation of methyl methacrylate using TTC-2 as the RAFT agent and ACHN as the initiator. Colour becomes lighter as experiment number increases.

Figure S29. NMR spectra for the 19 experiments completed for the RAFT polymerisation of methyl methacrylate using TTC-2 as the RAFT agent and ACHN as the initiator. Experiment number increases from bottom to top

Experiment number	Integral (6.6 – 4.9)	Integral (2.17 – 0.0)	Conversion (%)
1	217.71	353.84	4.77
2	179.72	399.39	22.42
3	183.90	396.69	20.81
4	203.31	375.93	12.25
5	170.63	414.09	27.05
6	173.51	408.56	25.48
7	140.33	442.89	39.85
8	128.93	448.47	44.17
9	164.01	417.34	29.47
10	144.26	438.65	38.13
11	130.24	450.65	43.95
12	136.06	446.91	41.65
13	134.46	448.45	42.33
14	127.30	449.64	44.84
15	121.59	457.86	47.54
16	127.84	456.13	45.27
17	136.86	450.14	41.71

Table S12. Integrals and conversion obtained for the 17 experiments completed for the RAFT polymerisation of methyl methacrylate using TTC-2 as the RAFT agent and ACHN as the initiator.