Supplementary Material (ESI) for Polymer Chemistry

Electronic Supporting Information

Assessment of SET-LRP in DMSO using Online Monitoring and Rapid GPC

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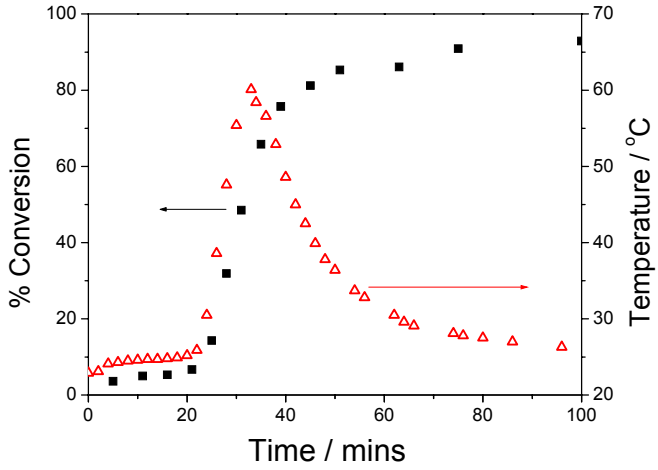

Figure SI1. Profile of conversion and temperature versus time for the Cu(0) wire / Me_6TREN catalysed polymerisation of MA at 50% solids in DMSO initiated by ethyl 2-bromoisobutyrate, mediated by 30 cm copper wire, 1 eq. Me_6TREN, [M] / [I] / [1] = 100 / 1 / 1. (**L1**)

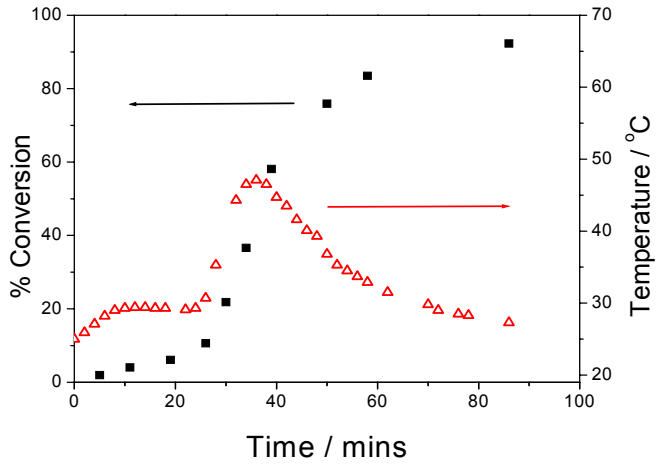

Figure SI2. Profile of conversion and temperature versus time for the Cu(0) wire / Me_6TREN catalysed polymerisation of MA at 50% solids in DMSO initiated by ethyl 2-bromoisobutyrate, mediated by 15 cm copper wire, 1 eq. ligand, [M] / [I] / [L] = 100 /1 /1. (**L2**)

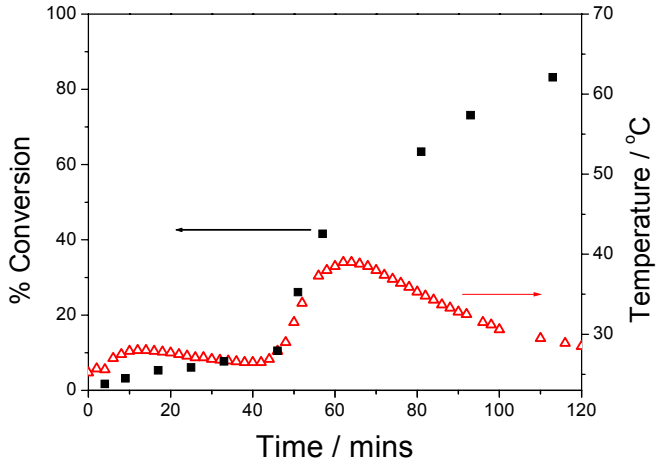

Figure SI3. Profile of conversion and temperature versus time for the Cu(0) wire / Me_6TREN catalysed polymerisation of MA at 50% solids in DMSO initiated by ethyl 2-bromoisobutyrate, mediated by 5 cm copper wire, 1eq ligand, [M] / [I] /L] = 100 / 1 / 1. (**L3**)

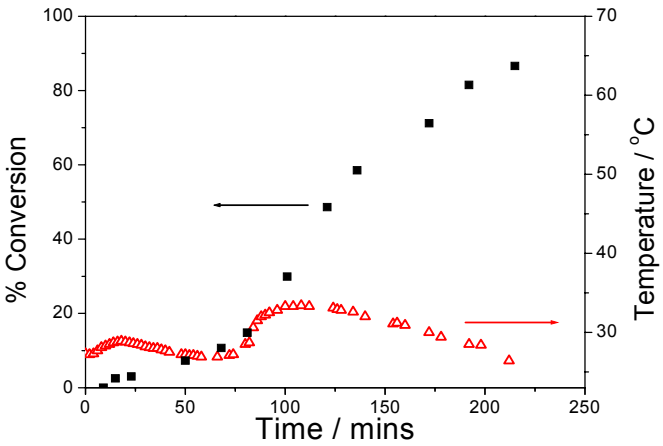

Figure SI4. Profile of conversion and temperature versus time for the Cu(0) / Me_6TREN catalysed polymerisation of MA at 50% solids in DMSO initiated by ethyl 2-bromoisobutyrate, mediated by 2.5 cm copper wire, [M] / [I] / [L] = 100 / 1 / 1. (**L4**)

Time / mins	% Conversion (NMR)	M_n / g mol^{-1}	M_w / g mol^{-1}	M_w / M_n
6	2	-	-	-
11	8	1960	3330	1.70
16	16	2130	3850	1.81
22	29	2970	3810	1.28
33	51	4790	5090	1.06
40	61	5920	6270	1.06
49	69	6730	7200	1.07
69	80	7710	8540	1.11
101	89	8100	8940	1.10
130	93	8470	9000	1.06

Table SI1. Conversion and molecular weight data for the Cu(0) wire / Me_6TREN catalysed polymerisation of MA in DMSO in the presence of CuBr initiated by ethyl 2-bromoisobutyrate at 25 °C. Ratio [M] / [I] [Cu] / [L] / [CuBr] = 100 / 1 / 1 / 1 / 0.5. Reaction performed at 50% solids. (**T4**)

Time / mins	% Conversion (NMR)	M_n / g mol^{-1}	M_w / g mol^{-1}	M_w / M_n
3	2	--		--
7	6	34	35	1.03
11	11	1420	2740	1.93
13.5	24	2380	3360	1.41
15	50	5590	6820	1.22
17	89	10100	12300	1.22
21	91	12200	14900	1.22
36	90	12100	14200	1.18

Table SI2. Conversion and molecular weight data for the Cu(0) powder / Me_6TREN catalysed polymerisation of MA in DMSO initiated by ethyl 2-bromoisobutyrate at 25 °C. Reaction performed at 66% solids, ratio [M] / [I] / [Cu] /[L] = 100 / 1 / 1 / 1. (**T7**)

Time / mins	% Conversion (NMR)	M_n / g mol^{-1}	M_w / g mol^{-1}	M_w / M_n
3	38			
7	48	1890	3870	2.05
13	84	11200	12600	1.13
31	96	11800	14000	1.19

Table SI3. Conversion and molecular weight data for the Cu(0) powder / Me_6TREN catalysed polymerisation of MA in DMSO initiated by ethyl 2-bromoisobutyrate at 25 °C in the presence of 1 eq $CuBr_2$. Reaction performed at 66% solids, ratio [M] / [I] / [Cu] / [$CuBr_2$] / [L] = 100 / 1 / 1 / 1 / 1. (**T6**)

Monitoring via Rapid GPC

Offline Data

Time / mins	% Conversion (NMR)	M_n / g mol^{-1}	M_w / g mol^{-1}	M_w / M_n
26	1.8	-	-	-
38	2.5	-	-	-
47	2.2	-	-	-
57	3.1	-	-	-
68	8.9	-	-	-
91	73.6	2310	7170	3.10
99	79.9	1850	2260	1.22
112	86.8	3760	4150	1.10
124	89.9	4210	4620	1.10
178	97.1	5260	5660	1.08

Table SI4. Offline data from manual sampling for the Cu(0) wire / Me_6TREN catalysed polymerisation of MA in DMSO initiated by ethyl 2-bromoisobutyrate. Reaction carried out at 25 ^{o}C, 50% solids, ratio [M] / [I] = 50 / 1 and mediated by 8 cm of wire (**D1**)

Time / mins	% Conversion	M_n / g mol^{-1}	M_w / g mol^{-1}	M_w / M_n
13	3.1	-	-	-
26	3.4	978	1350	1.38
37	9.4	2390	2890	1.21
45	34.2	3490	4470	1.28
56	56.5	5000	5620	1.13
66	72.5	6300	6960	1.10
85	83.1	7360	8080	1.10
100	89.0	7930	8660	1.09
180	95.6	8060	8670	1.08

Table SI5. Conversion and molecular weight data obtained offline from manual sampling for the Cu(0) wire / Me_6TREN catalysed polymerisation of MA in DMSO initiated by ethyl 2-bromoisobutyrate at 25 °C. Reaction performed at 50% solids, ratio [M] / [I] = 100 and mediated by 8 cm of wire. (**D2**)

Time / mins	% Conversion (NMR)	M_n / g mol^{-1}	M_w / g mol^{-1}	M_w / M_n
8	3.8	-	-	-
16	5.2	-	-	-
26	19.1	3630	4710	1.30
34	48.9	8440	9300	1.10
46	64.8	11700	12600	1.08
58	74.3	12600	13500	1.07
68	78.9	12800	13800	1.08

82	83.6	13000	14200	1.09
110	85.7	16200	17100	1.06
147	89.8	16200	17200	1.06
211	94.6	16800	17900	1.07

Table SI6. Offline data from manual sampling for the Cu(0) wire / Me_6TREN catalysed polymerisation of MA in DMSO initiated by ethyl 2-bromoisobutyrate. Reaction carried out at 25 ^{o}C, 50% solids, ratio [M] / [I] = 200 / 1 and mediated by 8 cm of wire. (**D3**)

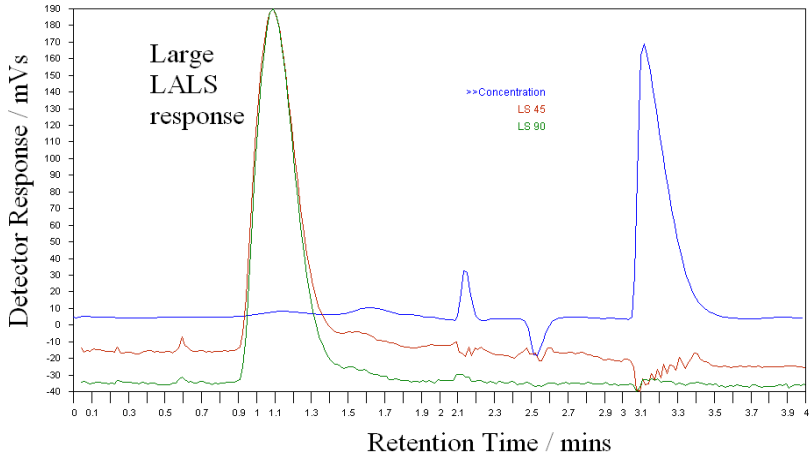

Figure SI5. Raw light scattering data for the Cu(0) wire / Me_6TREN mediated polymerisation of MA in DMSO initated by EBrB, corresponding to t = 50. This chromatogram corresponds to a reaction which reached a lower than expected experimentally determined molecular weight, described in the supporting information. The LALS detector shows the presence of a high molecular weight species.

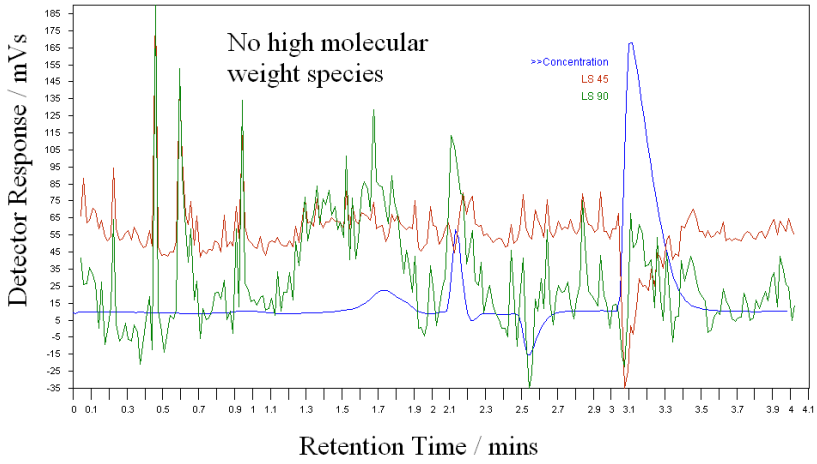

Figure SI6. Raw light scattering data for the Cu(0) wire / Me_6TREN catalysed polymerisation of MA in DMSO initiated by EBrB. The trace corresponds to t = 54 of the reaction described in this paper. There is no strong response from the dual angle LALS detector indicating that no high molecular weight polymer has formed. This reaction formed a polymer with M_n experimentally determined to be 8,060 g·mol^{-1}, in agreement with the theoretical value.

Methyl acrylate can polymerise in the presence of DMSO, copper wire, Me_6TREN but in the absence of initiator after deoxygenating via four freeze-pump thaw cycles and being left to stand in a thermostated oil bath at 25 °C for two hours. The polymer formed has a high molecular weight and broad polydispersity, Figure SI7, and bears a strong resemblance to the contaminant observed in SET-LRP polymerisations in DMSO. We propose that free-radical chain growth occurs prior to the formation of Cu nanoparticles that mediate the reaction. The appearance of a high molecular weight contaminant is more commonly observed in reactions with a large exotherm.

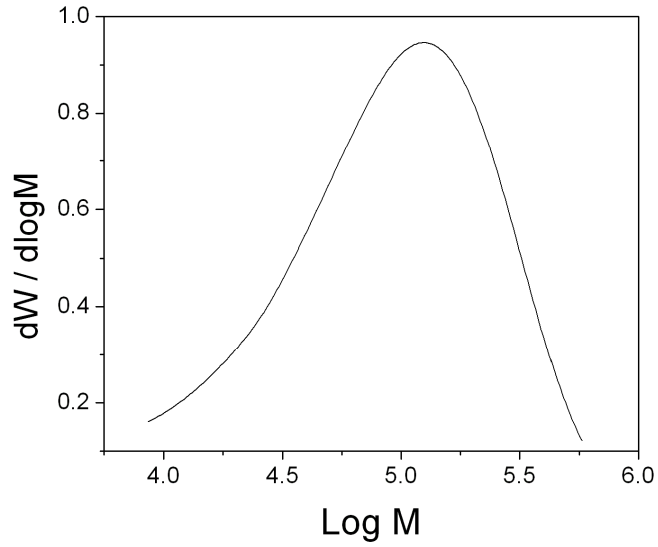

Figure SI7. GPC of the high molecular weight fraction of MA in DMSO mediated by 15 cm copper wire initiated by EBrB at 25 °C.

Calculation of the dn/dc value of poly(methyl acrylate)

The dn/dc value of Poly(methyl acrylate) in THF was determined to be 0.048 mL / g using PL Cirrus software.

Response (dRI detector) = $K^{DR} \times c \times dn/dc$

Where K^{DRI} is a detector constant, *c* is the concentration and *dn/dc* is the refractive index.

A detector constant for the dRI detector was determined by injecting a series of samples of poly(methyl methacrylate) at a range of concentrations in THF. This constant was obtained from measuring detector response with respect to concentration. This detector constant was then used when a sample of P(MA) of known / measured concentration was injected into the instrument. The PL Cirrus software then back calculated dn/dc.