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SUPPORTING INFORMATION

Insights into Relevant Mechanistic Aspects about the Induction Period of Cu^0 / Me_6TREN - Mediated Reversible - Deactivation Radical Polymerization

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EXPERIMENTAL SECTION

Materials and Methods: Methyl acrylate (MA, 99%, Aldrich), ethyl α-bromoisobutyrate (EBriB, 98%, Aldrich), copper(I) chloride(CuCl, 97%, Aldrich), copper(II) bromide ($CuBr_2$, 99%, Aldrich), Dimethyl sulfoxide (DMSO, 99.5%, Aldrich) and tris[2-(dimethylamino)ethyl]amine (Me_6TREN, 97%, Aldrich) were used as received . Cu(0)-wire (diameter 1 mm) was purchased from Sigma-Aldrich and was treated as stated in following section. Other solvents were purchased from Fisher Scientific and used as received.

Weight average molecular weight (M_w), number average molecular weight (M_n) and polydispersity (M_w/M_n) were obtained by SEC (Agilent GPC/SEC 50) equipped with an RI and LS detectors. The columns (30 cm PLgel Mixed-C, two in series) were eluted using tetrahydrofuran (THF) and calibrated using a series of 12 near-monodisperse PMMA standards (M_p from 690 to 1,944,000 g/mol). The polymers were analyzed in THF at a concentration of 5.0 mg/ml. All calibrations and analyses were performed at 40 ^oC and a flow rate of 1 ml/min. ^1H NMR analysis was carried out on a Varian NMR system 400 MHz spectrometer with MestRenova 6.1 processing software and reported in parts per million (ppm) relative to the response of the $CDCl_3$ (7.26 ppm) and tetramethylsilane (0.00 ppm).

Synthesis of PMA catalyzed by untreated Cu^0 wire/Me_6TREN: MA (100 mmol, 100 equiv), EBriB (1 mmol, 1 equiv), Me_6TREN (0.18 mmol, 0.18 equiv) and DMSO (9 ml) were added into the flask and oxygen was removed by bubbling argon through the solutions for 20 min at room temperature. Cu^0-wire (5 cm) was wrapped on the stirring bar as received and the solution was stirred at 600 rpm and the polymerization was conducted at 25 °C in an oil bath for the desired reaction time.

Synthesis of PMA catalyzed by pre-equilibrated Cu^0 wire/Me_6TREN: Two copy of same MA (100 mmol, 100 equiv), EBriB (1 mmol, 1 equiv), Me_6TREN (0.18 mmol, 0.18 equiv) and DMSO (9 ml) were added into two flasks and oxygen was removed by bubbling argon through the solutions for 20 min at room temperature. Cu^0-wire (5 cm) was wrapped on the stirring bar as received and immersed into one of the degassed flasks. the solution was stirred at 600 rpm at 25 °C in an oil bath for 30 min. After a brief rinse with DMSO, the stirring bar wrapped with copper wire was transferred to another freshly degassed flask. The solution was stirred at 600 rpm and the polymerization was conducted at 25 °C in an oil bath for the desired reaction time.

Synthesis of PMA catalyzed by hydrazine hydrate treated Cu^0 wire/Me_6TREN: Two copy of same MA (100 mmol, 100 equiv), EBriB (1 mmol, 1 equiv), Me_6TREN (0.18 mmol, 0.18 equiv) and DMSO (9 ml) were added into two flasks and oxygen was removed by bubbling argon through the solutions for 20 min at room temperature. Hydrazine hydrate (10.3 mM), and DMSO (2 mL) was added into a 25 ml flask under argon and bubbled by argon for 20 min. Cu^0-wire (5 cm) wrapped on the stirring bar was added to the hydrazine/DMSO mixture and was stirred for 30 min. The wire was rinsed with 10 mL of distilled THF followed by ethanol under positive argon pressure， then dried under vacuum. The activated Cu^0 was immersed into the degassed flasks.

The solution was stirred at 600 rpm and the polymerization was conducted at 25 °C in an oil bath for the desired reaction time.

Synthesis of PMA catalyzed by hydrochloric acid treated Cu^0 wire/Me_6TREN: MA (100 mmol, 100 equiv), EBriB (1 mmol, 1 equiv), Me_6TREN (0.18 mmol, 0.18 equiv) and DMSO (9 ml) were added into the flask and oxygen was removed by bubbling argon through the solutions for 20 min at room temperature. Cu^0-wire (5 cm) was immersed in conc. HCl and then thoroughly rinsed with acetone and water before used. The solution was stirred at 600 rpm and the polymerization was conducted at 25 °C in an oil bath for the desired reaction time.

Synthesis of PMA catalyzed by Cu^0 wire/Cu^{II}/Me_6TREN: MA (100 mmol, 100 equiv), EBriB (1 mmol, 1 equiv), Me_6TREN (0.18 mmol, 0.18 equiv) and DMSO (9 ml) were added into the flask and oxygen was removed by bubbling argon through the solutions for 20 min at room temperature. Cu^0-wire (5 cm) was immersed in conc. HCl and then thoroughly rinsed with acetone and water. The solution was stirred at 600 rpm and the polymerization was conducted at 25 °C in an oil bath for the desired reaction time.

Synthesis of PMA catalyzed by Cu^I/Me_6TREN: MA (100 mmol, 100 equiv), EBriB (1 mmol, 1 equiv), Me_6TREN (0.18 mmol, 0.18 equiv) and DMSO (9 ml) were added into the flask and oxygen was removed by bubbling argon through the solutions for 20 min at room temperature. CuCl (0.18 mmol, 0.18 equiv) was added and the solution was stirred at 600 rpm and the polymerization was conducted at 25 °C in an oil bath for the desired reaction time.

Synthesis of PMA catalyzed by Cu^0 wire/Cu^I/Me_6TREN: MA (100 mmol, 100 equiv), EBriB (1 mmol, 1 equiv), Me_6TREN (0.18 mmol, 0.18 equiv) and DMSO (9 ml) were added into the flask and oxygen was removed by bubbling argon through the solutions for 20 min at room temperature. Cu^0-wire (5 cm) was immersed in conc. HCl and then thoroughly rinsed with acetone and water. Cu^0 wire and CuCl (0.18 mmol, 0.18 equiv) were added and the solution solution was stirred at 600 rpm and the polymerization was conducted at 25 °C in an oil bath for the desired reaction time.

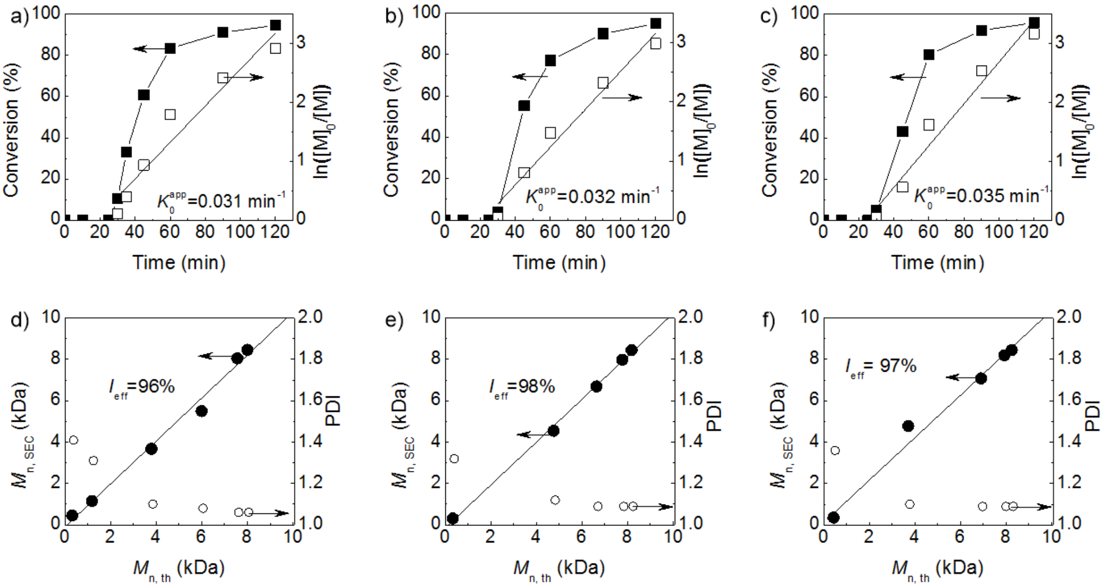

Figure S1. Kinetic plots of conversion and $\ln([M]_0/[M])$ versus time (a, b, c), and plots of number-average molecular weights ($M_{n, SEC}$) and PDI versus theoretical number-average molecular weights ($M_{n, th}$) (d, e, f) for polymerization of MA catalyzed by acid treated Cu^0 wire (a, d), hydrazine hydrate treated Cu^0 wire (b, e) or pre-equilibrated Cu^0 wire (c, f), with Me_6TREN as ligand in DMSO at 25 °C.

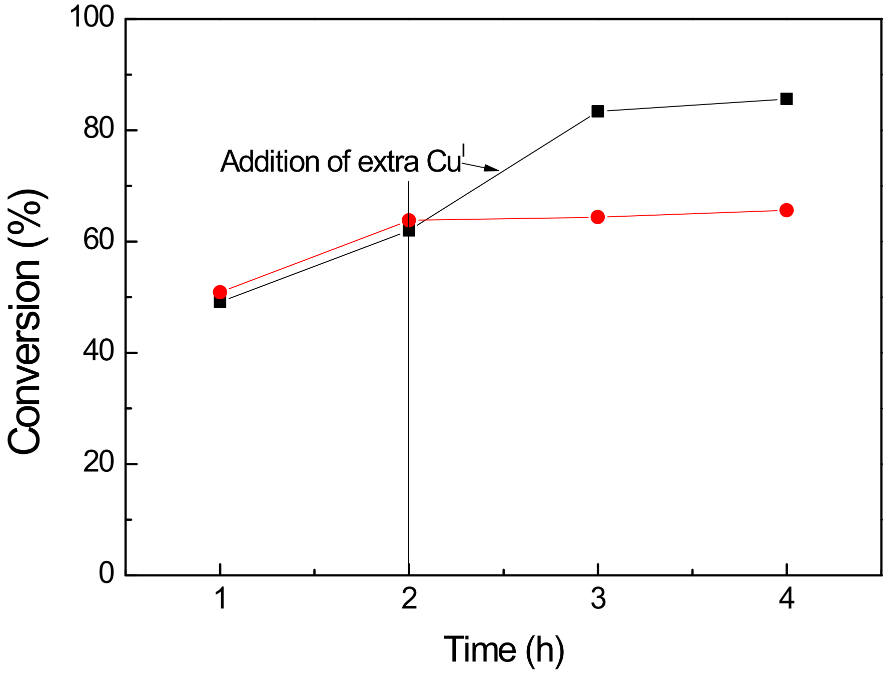

Figure S2. Kinetic plots of conversion versus time for polymerization of MA catalyzed by Cu^I with Me_6TREN as ligand in DMSO at 25 °C.

Table S1. Reaction results for the Cu^0 – mediated RDRP with different treatment of copper wire[a]

	Catalyst	**Time [min]**	**$M_{n,th}$ [b] [kDa]**	**$M_{n,SEC}$ [c] [kDa]**	**PDI[c]**	**Conv[b] [%]**
1	Cu^0 [d]	30	0.89	0.86	1.41	10
2		35	2.84	2.29	1.11	33
3		45	5.23	5.06	1.10	60
4		60	7.17	7.47	1.09	83
5		90	7.84	7.96	1.09	91
6		120	8.14	8.20	1.09	95
22	Cu^0 [e]	30	0.33	0.31	1.32	3
23		45	4.76	4.55	1.12	55
24		60	6.64	6.7	1.09	77
25		90	7.77	7.98	1.09	90
26		120	8.18	8.45	1.09	95
27	Cu^0 [f]	30	0.43	0.36	1.36	5
28		45	3.71	4.78	1.10	43
29		60	6.91	7.08	1.09	80
30		90	7.93	8.20	1.09	92
31		120	8.25	8.45	1.09	96

[a] Reaction condition: [M] : [I] : [L] = 100 : 1 : 0.18, [M] = 5.50 M; M = MA, I = Ethyl α-bromoisobutyrate (EBriB), Solvent = DMSO, T = 25 °C; [b] $M_{n,th}$ and Monomer conversion was confirmed using ^1H NMR; [c] $M_{n,SEC}$ and PDI were characterized using size exclusion chromatography (SEC) with an RI detector; [d] copper wire was untreated. [e] Copper wire was activated by hydrazine hydrate; [f] Copper wire was pre-equilibrated.

Table S2. Reaction results for the polymerization using different valent coppers in presence of Me_6TREN as ligand [a]

	Catalyst[b]	**Time [min]**	**$M_{n,th}$**[c] **[kDa]**	**$M_{n,SEC}$**[d] **[kDa]**	**PDI**[d]	**Conv**[c] **[%]**
1	Cu^0	30	0.31	0.45	1.41	3
2		35	1.18	1.15	1.31	14
3		45	3.79	3.68	1.10	44
4		60	5.99	5.50	1.08	70
5		90	7.56	8.05	1.06	88
6		120	8.00	8.46	1.06	93
7	Cu^0&Cu^{II}	10	1.67	1.47	1.44	19
8		30	5.60	5.89	1.04	65
9		60	7.26	7.21	1.03	84
10		90	7.85	7.83	1.03	91
11		120	8.18	8.21	1.04	95
12	Cu^I	5	2.61	2.31	1.13	31
13		10	2.91	2.40	1.11	34
14		30	3.72	3.43	1.10	43
15		45	4.05	3.49	1.09	47
16		60	4.69	4.38	1.09	48
17		120	4.70	4.70	1.08	54
18	Cu^0&Cu^I	10	2.30	2.16	1.16	27
19		30	4.83	4.48	1.13	56
20		60	6.53	6.51	1.08	76
21		120	7.66	7.62	1.07	89

[a] Reaction condition: [M] : [I] : [L] = 100 : 1 : 0.18, [M] = 5.50 M; M = MA, I = ethyl α-bromoisobutyrate (EBriB), Solvent = DMSO, $T = 25\ ^{o}C$; [b] Cu^0 wire (l = 5 cm, d = 1 mm) was pre-treated with hydrochloric acid and thoroughly rinsed with acetone and distilled water, Cu^I is 0.18 equiv. relative to EBriB (equal to Me_6TREN), Cu^{II} is 0.05 equiv. relative to EBriB; [c] $M_{n,th}$ and monomer conversion was confirmed using ^1H NMR; [d] $M_{n,SEC}$ and PDI were characterized using size exclusion chromatography (SEC) equipped with an RI detector.