Supporting Information to

Reversible-Deactivation Radical Polymerization Mediated by CuSO₄•5H₂O: an Alternative and Promising Copper(II)-Based Catalyst

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Experimental part:

Materials

Methyl methacrylate (MMA) (>99%), methyl acrylate (MA) (>99%), styrene (St) (>99%), were purchased from Shanghai Chemical Reagents Co. (Shanghai, China). The monomers were washed three times with an aqueous solution of sodium hydroxide (5%wt), followed by washes with deionized water until the solution was neutralized. The resulting solution was then dried over anhydrous magnesium sulfate, distilled twice at reduced pressure, 2-(dimethylamino)ethyl methacrylate (DMAEMA) (>99%) was purchased from Aldrich, it was passed through basic alumina columns, then vacuum-distilled from CaH₂, and all of them were stored at -18 °C. N,N,N',N'',Pentamethyldiethylenetriamine (PMDETA) (98%, Jiangsu Liyang Jiangdian Chemical Factory, China) was dried with 4 Å molecular sieves and distilled under vacuum. Tris-(2-dimethylaminoethyl) amine (Me₆TREN) was synthesized as described in the literature.¹ 2,2'-bipyridine (bpy) (99%), and tri(3,6-dioxaheptyl) amine (TDA-1) (97%) were purchased from Shanghai Chemical Reagents and used as received. Zero-valent iron powder (Fe(0), <200 mesh, 99%, metals basis), and iron wire (99.9%) were purchased from Alfa Aesar and used as received. Copper(II) suflate pentahydrate (CuSO₄·5H₂O) (99%), copper(II) bromide (CuBr₂, 98.5%), ascorbic acid (AA) (99.9%, Shanghai guanghua Chemical Factory, China), 2,2-dichloroacetophenone (DCAP) (97%, Alfa Aesar Co.), methyl 2-bromopropionate (MBP) (97%, Alfa Aesar Co.), ethyl 2-bromoisobutyrate (EBiB) (98%, Acros), methyl alpha-bromophenylacetate (MBPA) (97%, J & K Scientific LTD.), dimethyl sulfoxide (DMSO) (99.9%, Shanghai Chemical Reagents Co.), *N,N*-dimethylformamide (DMF) (99.9%, Shanghai Chemical Reagents Co.), n-methyl-2-pyrrolidone (NMP) (98%, Sinopharm Chemical Reagents Co.), toluene (99.5%, Nanjing Chemical Reagents Co.) and anisole (98%, Sinopharm Chemical Reagents Co.) were used as received. All other chemicals were obtained from Shanghai Chemical Reagents Co. and used as received unless mentioned.

Characterization

The number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) of the polymers were determined using a Waters 1515 size exclusion chromatography (SEC) equipped with a refractive-index detector (Waters 2412), using HR 1 (pore size: 100 Å, 100-5000 Da), HR 2 (pore size: 500 Å, 500-20,000 Da), and HR 4 (pore size 10,000 Å, 50-100 000 Da) columns (7.8 × 300 mm, 5 µm beads size) with molecular weights ranging from 0.1 to 500 kg/mol. For PMMA, PMA and PS samples, THF was used as the eluent at a flow rate of 1.0 mL/min and 30 °C. SEC samples were injected using a Waters 717 plus autosampler and calibrated with poly(methylmethacrylate) standards for PMMA, PMA and PDMAEMA and poly(styrene) standards for PS purchased from Waters. The apparent SEC values were subjected to correction by using Mark–Houwink–Kuhn–Sakurada (MHKS) parameters with equation: Log(MW_{MA}) = 0.105+0.956Log(MW_{MMA}).² For PDMAEMA samples, DMF was used as the eluent at a flow rate of 1.0 mL/min and 35 °C. The apparent SEC values were subjected to correction by multiplying of an approximate factor of 1.5 according to literature.³ The ¹H NMR spectrum of the precipitated polymer was recorded on an INOVA 400 MHz nuclear magnetic resonance instrument using CDCl₃ as the solvent and tetramethylsilane (TMS) as an internal standard. The UV-vis spectra were recorded on a Shimadzu UV-3150 spectrophotometer.

The UV-Vis spectroscopic analyses of Fe/CuSO₄·5H₂O/PMDETA complex in DMSO at different time

Fe(0) (1.3 mg), CuSO₄·5H₂O (2.9 mg) and PMDETA (4.9 μ L) were placed in a quartz UV-vis cell (1 mm path length), And another, without Fe(0), that is CuSO₄·5H₂O (2.9 mg) and PMDETA (4.9 μ L), then supplement to 3 mL with dimethyl sulfoxide (DMSO) for each, all systems were deoxygenated. After vigorous shaking, the cells were placed in the UV-vis spectrometer for measurement. Then the cells were put into a water bath equipped with a thermostat at 25 ± 1 °C for reaction and get out for measurement after a preset time, the absorbance was recorded in the 200-900 nm range.

Typical procedures for the polymerization of MMA

typical polymerization procedure with DMSO the solvent for the ratio of А as $[MMA]_0/[DCAP]_0/[Fe(0)]_0/[CuSO_4 \cdot 5H_2O]_0/[PMDETA]_0 = 200/1/1/0.5/1$ is as follows. The monomer (MMA, 1.0 mL, 9.4 mmol), solvent (DMSO, 1.0 mL), initiator (DCAP, 6.7 µL, 0.0472 mmol), catalyst (CuSO₄·5H₂O, 5.9 mg, 0.0236 mmol), and ligand (PMDETA, 9.8 µL, 0.0472 mmol), reducing agent (Fe(0), 2.6 mg, 0.0472 mmol) were added to a 5.0 mL ampule in the following order: catalyst, monomer, ligand, solvent, initiator, and then reductant. The solution deoxygenated with six standard freeze - pump thaw cycles. The ampoule was then flame sealed and placed in a stirred water bath equipped with a thermostat at 25 ± 1 °C. After 2.5 hours, the ampule was cooled by immersion in ice water. Afterward, the ampule was opened, and the contents were dissolved in 5.0 mL of THF and passed through a small basic Al₂O₃ chromatographic column to remove Cu and Fe compounds. The resulting solution was precipitated into 200 mL of cold methanol with stirring. The polymer was isolated by filtration and dried under

vacuum until a constant weight was recorded at room temperature. The monomer conversion was 35.7% determined by gravimetrical calculation. The M_n and M_w/M_n values were determined by SEC (THF) with poly(methylmethacrylate) (PMMA) standards ($M_{n,SEC} = 12.8$ kg/mol, $M_w/M_n = 1.31$).

Chain extension with PMMA as a macroinitiator

A predetermined quantity of obtained PMMA was added to a dried ampoule and then the predetermined quantity of MMA, Fe(0), $CuSO_4 \cdot 5H_2O$, PMDETA and DMSO was added. The polymerization temperature was then stabilized at 25 ± 1 °C. The rest of the procedure was identical to that described earlier except that DCPA replaced by obtained PMMA.





Fig. S1. (a) Kinetic investigation $(\ln([M]_0/[M]))$ versus time) of methyl methacrylate (MMA) with toluene as solvent at various concentrations of AA. $[MMA]_0 = 4.71 \text{ mol/L}$, MMA/toluene = 1/1 (v/v), temperature = 80 °C. [M]₀ and [M] refer to the initial concentration of MMA and instant concentration of MMA, respectively. k_p^{app} refer to apparent rate constant of propagation. (b) Number average molecular weight (M_n) and molecular weight distribution (M_w/M_n) of poly(methylmethacrylate) (PMMA) versus the of conversion of MMA at various concentrations AA. (c) (d) $[MMA]_0/[EBiB]_0/[CuSO_4 \cdot 5H_2O]_0/[PMDETA]_0/[AA]_0$ 200/1/1/1/2. = $[MMA]_0/[EBiB]_0/[CuSO_4 \cdot 5H_2O]_0/[PMDETA]_0/[AA]_0$ 200/1/1/1/1 (Fig. 1). = (e) $[MMA]_0/[EBiB]_0/[CuSO_4 \cdot 5H_2O]_0/[PMDETA]_0/[AA]_0 = 200/1/1/1/0.$ (f) $[MMA]_0/[EBiB]_0/[CuBr_2]_0$ $[PMDETA]_0/[AA]_0 = 200/1/1/1/1$ (Fig. 2). Theoretical molecular weight $M_{n,th} = ([MMA]_0/[EBiB]_0) \times$ $M_{\rm MMA} \times {\rm Conversion} + M_{\rm EBiB}$.

Entry ^a	Catalyst	Time (h)	Con. (%)	M _{n,SEC} (kg/mol)	$M_{ m w}/M_{ m n}$	M _{n,NMR} (kg/mol)	FD
1	CuSO ₄ ·5H ₂ O	1.0	19.7	13.2	1.22	6.9	0.527
2	CuSO ₄ ·5H ₂ O	1.25	24.4	13.9	1.22	8.8	0.630
3	CuSO ₄ ·5H ₂ O	2.0	47.3	15.3	1.30	9.2	0.602
4	CuSO ₄ ·5H ₂ O	4.0	81.9	22.3	1.21	19.9	0.894
5	CuBr ₂	0.5	24.7	13.0	1.08	7.0	0.535
6	CuBr ₂	0.67	41.7	17.8	1.14	11.5	0.646
7	CuBr ₂	0.83	48.9	19.7	1.15	13.5	0.687
8	CuBr ₂	3	82.4	34.7	1.44	19.1	0.552

Table S1. The compared chain end functionalization degrees (FD) of polymers mediated by $CuSO_4 \cdot 5H_2O$ and $CuBr_2$.

^{a)}[MMA]₀/[EBiB]₀/[Catalyst]₀/[PMDETA]₀/[AA]₀ = 200/1/1/1/1, MMA = 1.0 mL; toluene = 1.0 mL, the polymerization temperature was 80 °C for all cases. MMA = methyl methacrylate; EBiB = ethyl 2-bromoisobutyrate; PMDETA = N,N,N',N",Pentamethyldiethylenetriamine. $M_{n,SEC}$ and M_w/M_n refer to the number-average molecular weight and molecular weight distribution by SEC, respectively. $M_{n,NMR}$ refer to the number-average molecular weight by ¹H NMR. FD = $M_{n,NMR}/M_{n,SEC}$.





Fig. S2. (a) Kinetic investigation $(\ln([M]_0/[M])$ versus time) of methyl methacrylate (MMA) with DMSO as solvent. [MMA]_0 =4.71mol/L, MMA/DMSO = 1/1 (v/v), temperature = 25 °C. [M]_0 and [M] refer to the initial concentration of MMA and instant concentration of MMA, respectively. k_p^{app} refer to apparent rate constant of propagation. (b) Number average molecular weight (M_n) and molecular weight distribution (M_w/M_n) of poly(methylmethacrylate) (PMMA) versus the conversion of MMA at various molar ratios of [Fe(0)]_0/[CuSO_4·5H_2O]_0. (c) [MMA]_0/[DCAP]_0/[Fe(0)]_0/[CuSO_4·5H_2O]_0/[PMDETA]_0 = 200/1/1/0.5/1. (d) [MMA]_0/[DCAP]_0/[Fe(0)]_0/[CuSO_4·5H_2O]_0/[PMDETA]_0 = 200/1/1/1. (e) [MMA]_0/[DCAP]_0/[Fe(0)]_0/[CuSO_4·5H_2O]_0/[PMDETA]_0 = 200/1/1/1. (for $M_{n,th} = ([MMA]_0/[DCAP]_0) \times M_{MMA} \times Conversion + M_{DCAP}$.



Fig. S3. ¹H NMR spectrum of poly (methyl methacrylate) (PMMA, $M_{n,SEC} = 9.9 \text{ kg/mol}, M_w/M_n = 1.25$) obtained from [MMA]₀/[DCAP]₀/[Fe(0)]₀/[CuSO₄·5H₂O]₀/[PMDETA]₀ = 200/1/1/0.5/1. CDCl₃ was used as the solvent and tetramethylsilane (TMS) as the internal standard. $M_{n,SEC}$ and M_w/M_n refer to the number-average molecular weight and molecular weight distribution by SEC, respectively.



Fig. S4. SEC curves before and after chain extension in DMSO with poly (methyl methacrylate) (PMMA) (obtained from $[MMA]_0/[DCAP]_0/[Fe(0)]_0/[CuSO_4 \cdot 5H_2O]_0/[PMDETA]_0 = 200/1/1/0.5/1)$ as the macro-initiator at 25 °C. The condition of the chain-extension: $[MMA]_0/[PMMA]_0$ / $[Fe(0)]_0/[CuSO_4 \cdot 5H_2O]_0/[PMDETA]_0 = 500/1/3/5/6$, $[MMA]_0 = 1.95$ mol/L, MMA = 0.26 mL, DMSO = 1.0 mL, 6 h, 64.2% conversion.

Table S2. Polymerizations	s of St and	MA under	various	conditions.	a)
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Entry	Monomer		initiator	catalyst	Ligand	Time (h)	Con.	$M_{n,SEC}$	$M_{ m w}/M_{ m n}$	$M_{ m n,th}$
	(equiv)	solvent	(equiv)	(equiv)	(equiv)		(%)	(kg/mol)		(kg/mol)
1	St (200)	DMSO	MBP(1)	Fe(0)/CuSO ₄ ·5H ₂ O (1/0.5)	TDA -1(1)	12.0	2.9	38.7	1.92	0.7
2	St (200)	DMSO	MBP(1)	Fe(0)/CuSO ₄ ·5H ₂ O (1/0.5)	TDA -1(1)	112.0	49.6	31.9	2.29	10.1
3	St (200)	DMF	MBP(1)	Fe(0)/CuSO ₄ ·5H ₂ O (1/0.5)	PMDETA(1)	24.0	14.4	3.6	1.12	3.1
4	St (200)	DMF	MBP(1)	Fe(0)/CuSO ₄ ·5H ₂ O (1/0.5)	PMDETA(1)	124.0	44.7	10.4	1.19	9.5
5	St (200)	NMP	MBP (1)	Fe(0)/CuSO ₄ ·5H ₂ O (1/0.5)	PMDETA(1)	32.0	15.2	3.8	1.73	3.2
6	St (200)	NMP	MBP(1)	Fe(0)/CuSO ₄ ·5H ₂ O (1/0.5)	PMDETA(1)	96.0	40.2	6.4	1.29	8.2
7	St (200)	anisole	MBP(1)	Fe(0)/CuSO ₄ ·5H ₂ O (1/0.5)	PMDETA(1)	57.0	32.3	6.4	1.27	6.6
8	St (200)	anisole	MBP(1)	Fe(0)/CuSO ₄ ·5H ₂ O (1/0.5)	PMDETA(1)	95.0	35.5	9.5	1.73	7.3
9	St (200)	toluene	MBP(1)	Fe(0)/CuSO ₄ ·5H ₂ O (1/0.5)	PMDETA(1)	57.0	14.3	4.0	1.24	3.0
10	St (200)	toluene	MBP(1)	Fe(0)/CuSO ₄ ·5H ₂ O (1/0.5)	PMDETA(1)	167.0	39.6	8.6	1.16	8.1
11	MA (200)	DMSO	MBP(1)	Fe(0)/CuSO ₄ ·5H ₂ O (1/0.5)	TDA-1 (1)	8.0	23.3	45.7	1.98	3.8
12	MA (200)	DMSO	MBP(1)	Fe(0)/CuSO ₄ ·5H ₂ O (1/0.5)	TDA-1 (1)	32.0	59.2	50.1	1.78	10.4
13	MA (200)	DMF	MBP (1)	Fe(0)/CuSO ₄ ·5H ₂ O (1/0.5)	PMDETA(1)	6.0	36.6	17.3	1.59	6.5
14	MA (200)	DMF	MBP(1)	Fe(0)/CuSO ₄ ·5H ₂ O (1/0.5)	PMDETA(1)	12.0	65.7	14.4	1.41	11.4
15	MA (200)	NMP	MBP(1)	Fe(0)/CuSO ₄ ·5H ₂ O (1/0.5)	PMDETA(1)	1.0	36.9	95.5	1.52	6.5
16	MA (200)	NMP	MBP(1)	Fe(0)/CuSO ₄ ·5H ₂ O (1/0.5)	PMDETA(1)	6.0	88.6	102.3	1.47	15.4
17	MA (200)	anisole	MBP(1)	Fe(0)/CuSO ₄ ·5H ₂ O (1/0.5)	PMDETA(1)	32	0.0			
18	MA (200)	anisole	MBP (1)	Fe(0)/CuSO ₄ ·5H ₂ O (1/0.5)	PMDETA(1)	298	0.0			
19	MA (200)	toluene	MBP(1)	Fe(0)/CuSO ₄ ·5H ₂ O (1/0.5)	PMDETA(1)	32	0.0			
20	MA (200)	toluene	MBP(1)	Fe(0)/CuSO ₄ ·5H ₂ O (1/0.5)	PMDETA(1)	298	0.0			

^{a)}All polymerizations were conducted with MA (or St) = 1.0 mL, temperature = 25 °C, solvent = 1.0 mL. MA = methyl acrylate; St = styrene; MBP = methyl 2-bromopropionate; PMDETA = N,N,N',N'',N'',Pentamethyldiethylenetriamine; TDA-1 = tris-(3,6-dioxa-heptyl) amine; DMSO = dimethyl sulfoxide; DMF = N,N-dimethylformamide; NMP = N-methyl-2-pyrrolidone. $M_{n,SEC}$ and M_w/M_n refer to the number-average molecular weight and molecular weight distribution by SEC, respectively. $M_{n,th}$ (PMA) = ([MA]_0/[MBP]_0) × M_{MMA} × Conversion + M_{MBP} ; $M_{n,th}$ (PSt) = ([St]/[MBP]_0) × M_{St} × Conversion + M_{MBP} .



Fig. S5. (a) Kinetic investigation $(\ln([M]_0/[M]))$ versus time) of methyl acrylate (MA) with DMSO as solvent. $[MA]_0 = 5.55 \text{ mol/L}$, MA/DMSO = 1/1 (v/v), temperature = 25 °C. $[M]_0$ and [M] refer to the initial concentration of MA and instant concentration of MA, respectively. (b) Number average molecular weight (M_n) and molecular weight distribution (M_w/M_n) of poly(methyl acrylate) (PMA) versus the of MA $[Fe(0)]_0/[CuSO_4 \cdot 5H_2O]_0.$ conversion at various molar ratios of (c) $[MA]_0/[MBP]_0/[Fe(0)]_0/[CuSO_4 \cdot 5H_2O]_0/[PMDETA]_0$ 200/1/1/0.5/1 (d) = $[MA]_0/[MBP]_0/[Fe(0)]_0/[CuSO_4 \cdot 5H_2O]_0/[PMDETA]_0$ 200/1/1/1/1. = (e) $[MA]_0/[MBP]_0/[Fe(0)]_0/[CuSO_4 \cdot 5H_2O]_0/[PMDETA]_0 = 200/1/0.5/1/1$. Theoretical molecular weight $M_{n,th}$ = $([MA]_0/[MBP]_0) \times M_{MA} \times Conversion + M_{MBP}$.



Fig. S6. (a) Kinetic investigation $(\ln([M]_0/[M])$ versus time) of styrene (St) with DMSO as solvent. $[St]_0$ =4.35mol/L, St/DMSO = 1/1 (v/v), temperature = 25 °C. $[M]_0$ and [M] refer to the initial concentration of St and instant concentration of St, respectively. (b) Number average molecular weight (M_n) and molecular weight distribution (M_w/M_n) of poly(styrene) (PSt) versus the conversion of St at various molar ratios of $[Fe(0)]_0/[CuSO_4 \cdot 5H_2O]_0$. (c) $[St]_0/[MBP]_0/[Fe(0)]_0/[CuSO_4 \cdot 5H_2O]_0/[PMDETA]_0 = 200/1/1/0.5/1$ (d) $[St]_0/[MBP]_0/[Fe(0)]_0/[CuSO_4 \cdot 5H_2O]_0/[PMDETA]_0 = 200/1/1/1.$ (e) $[St]_0/[MBP]_0/[Fe(0)]_0/[CuSO_4 \cdot 5H_2O]_0/[PMDETA]_0 = 200/1/0.5/1/1.$ Theoretical molecular weight $M_{n,th} =$ $([St]_0/[MBP]_0) \times M_{St} \times Conversion + M_{MBP}.$



Fig. S7. ¹H NMR spectrum of poly (methyl acrylate) (PMA, $M_{n,SEC} = 13.2$ kg/mol, $M_w/M_n = 1.12$) obtained from the Fe(0)/CuSO₄.5H₂O mediated polymerization. CDCl₃ was used as the solvent and tetramethylsilane (TMS) as the internal standard. $M_{n,SEC}$ and M_w/M_n refer to the number-average molecular weight and molecular weight distribution by SEC, respectively.



Fig. S8. ¹H NMR spectrum of poly (styrene) (PSt, $M_{n,SEC} = 6.5$ kg/mol, $M_w/M_n = 1.10$) obtained from the Fe(0)/CuSO₄.5H₂O mediated polymerization. CDCl₃ was used as the solvent and tetramethylsilane

(TMS) as the internal standard. $M_{n,SEC}$ and M_w/M_n refer to the number-average molecular weight and molecular weight distribution by SEC, respectively.



Fig. S9. SEC curves before and after chain extension in DMSO with poly (methyl acrylate) (PMA) as the macro-initiator at 25 °C. The condition of the chain-extension: $[MA]_0/[PMA]_0/[Fe(0)]_0$ /[CuSO₄.5H₂O]₀/[PMDETA]₀ = 450/1/4/2/5, $[MA]_0$ = 1.85 mol/L, MA = 0.2 mL, DMSO = 1.0 mL, 10 h, 80.2% conversion.



Fig. S10. SEC curves before and after chain extension in DMSO with poly styrene (PSt) as the macro-initiator at 25 °C. The condition of the chain-extension: $[St]_0/[PSt]_0/[Fe(0)]_0$

 $/[CuSO_4.5H_2O]_0/[PMDETA]_0 = 450/1/4/2/5$, $[St]_0 = 1.51 \text{ mol/L}$, St = 0.2 mL, DMSO = 1.0 mL, 10 h, 10.2% conversion.



Fig. S11. (a) UV-Vis spectra of $[Fe(0)]_0/[CuSO_4 \cdot 5H_2O]_0 / [PMDETA]_0 = 0.024/0.012/0.024$ in DMSO changed over time; (b) UV-Vis spectra of $[CuSO_4 \cdot 5H_2O]_0/[PMDETA]_0 = 0.012/0.024$ in DMSO changed over time. Solvent = 3.0 mL, T = 25 °C. PMDETA = N,N,N',N'',Pentamethyldiethylenetriamine; DMSO = dimethyl sulfoxide.

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