Atom Transfer Radical Polymerization Enabled by Sonochemically Labile Cu-Carbonate Species

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Experimental section

Materials

All chemicals were purchased from Aldrich unless described in detail. All carbonates and bicarbonates were purchased from Fisher Scientific. Acrylate monomers were purified by passing through a column filled with basic alumina to remove the polymerization inhibitors. Tris(2-pyridiylmethyl)amine (TPMA, 98%) was kindly donated by Koei Chemical Co., Ltd. Tetraethylammonium tetrafluoroborate (Et_4NBF_4, Alfa Aesar, 99%), used as a supporting electrolyte for electrochemical analysis, was recrystallized from ethanol, and dried in a vacuum oven at 70 °C for 48 h. All other chemicals were used as received.

Instruments

^{1}H nuclear magnetic resonance (^{1}H NMR) measurements were performed on a Bruker Advance 300 MHz spectrometer with $CDCl_3$ or acetone-d6 as solvent. Gel permeation chromatography (GPC) was conducted with a Waters 515 pump and Waters 410 differential refractometer using PSS columns (Styrogel 105, 103, 102 Å) in THF as eluent at 35 °C and at a flow rate of 1 mL min^{-1}. The apparent molecular weights were determined using linear poly(methyl methacrylate) standards using WinGPC 7.0 software from PSS. Electrochemical studies on the Cu catalyst were carried out in a 5-neck electrochemical cell, equipped with three electrodes and connected to an Autolab PGSTAT302N potentiostat/galvanostat (Metrohm USA) run by a PC with NOVA 2.0 software. The three-electrode system was composed by: i) a Pt wire counter electrode (Metrohm); ii) an homemade reference electrode: Ag|AgI|(0.1 M *n*-Bu_4NI in DMF); iii) a glassy carbon (GC) disk electrode (3 mm dia., Metrohm), as working electrode (WE). Before each experiment, the disk was cleaned by polishing with a 0.25-μm diamond paste, followed by ultrasonic rinsing in ethanol for 5 min. Ferrocene (Fc) was added at the end of each experiment as an internal standard, to refer all potentials to the saturated calomel

electrode (SCE, $E°_{(Fc+|Fc)}$ = 0.449 V vs SCE in DMSO. The cell was thermostated at 25 °C, and all experiments were performed under inert atmosphere (N_2). Sono-ATRP was performed in an ultrasonic bath (Branson Ultrasonics CPX2800, 40 kHz, 110 W, contact area is 322 cm^2, 0.3 W/cm^{-2}). Before polymerization, the ultrasonic bath was switched on for 1 h to stabilize it.

General procedures

Procedure for sono-ATRP of methyl acrylate

Ethyl α-bromoisobutyrate (EBiB, 19.3 mg, 8.8 µmol), 74 µL of a 1/4 $CuBr_2$/TPMA (3.3 µmol $CuBr_2$, 13.2 µmol TPMA) stock solution (10 mg/mL), sodium carbonate (Na_2CO_3, 2.3 mg, 22 µmol), and 2 mL DMSO were added to a 10 mL Schlenk flask. The flask was sealed, and the oxygen was removed by N_2 bubbling for 30 min. Degassed methyl acrylate (MA, 2 mL, 22 mmol) was then added under N_2 flow. The flask was transferred to the ultrasonic bath to start the polymerization. Samples were withdrawn from the reaction by degassed syringes, at timed intervals, to measure the conversion by ^{1}H NMR and analyze the polymer by GPC to obtain number-average molecular weight (M_n) and dispersity.

Procedure for chain extension by ultrasound

EBiB (19.3 mg, 8.8 µmol), 74 µL of a 1/4 $CuBr_2$/TPMA (3.3 µmol $CuBr_2$, 13.2 µmol TPMA) stock solution (10 mg/mL), Na_2CO_3 (2.3 mg, 22 µmol), and 2 mL DMSO were added to a 10 mL Schlenk flask. The flask was sealed, and the oxygen was removed by N_2 bubbling for 30 min. Degassed MA (2 mL, 22 mmol) was then added under N_2 flow. The flask was transferred to the ultrasonic bath to start the polymerization. After 6 h of sonication, another 2 mL degassed MA was added. Samples were withdrawn from the reaction by degassed syringes, at timed intervals, to measure the conversion by ^{1}H NMR and analyze the polymer by GPC to obtain number-average molecular weight (M_n) and dispersity.

Table S1. Results for sodium carbonate catalyzed ATRP under ultrasound

Entry[a]	Monomer	DP_t	t (h)	Na_2CO_3 (wt%)	Conversion[b]	$M_{n,th}$[c]	$M_{n,GPC}$[d]	M_w/M_n[d]
1	MA	100	2	0.01	35%	3,205	3,300	1.18
2	MA	100	2	0.05	74%	6,559	6,500	1.13
3	MA	100	2	0.25	86%	7,591	7,400	1.16
4	MA	100	2	0	0	N/A	N/A	N/A
5[e]	MA	100	2	0.05	5%	625	N/A	N/A
6	MA	200	2	0.25	82%	14,300	12,900	1.08
7	MA	400	3	0.05	66%	22,900	22,100	1.06
8	MA	800	6	0.05	76%	52,480	48,200	1.05
9	EA	100	7	0.05	91%	9,300	9,100	1.11
10	EA	200	4	0.05	69%	14,000	14,200	1.08
11	$OEOA_{480}$	100	4	0.05	40%	19,200	15,000	1.23

[a]Reaction conditions: $[MA]_0:[EBiB]_0:[CuBr_2]_0:[TPMA]_0$ = 100:X:0.015:0.06 in 50% (v/v) DMSO, 0.05 wt% Na_2CO_3. Ultrasonic bath (25 °C ± 5 °C, 40 kHz, 110 W). [b]Conversion determined by ^1H NMR. [c]Calculated on the basis of conversion (i.e., $M_{n,th} = M_{EBiB} + [MA]_0/[EBiB]_0 \times \text{conversion} \times M_{MA}$). [d]Determined by GPC in THF, based on linear PMMA as calibration standard. [e] Without ultrasound, stirred at room temperature.

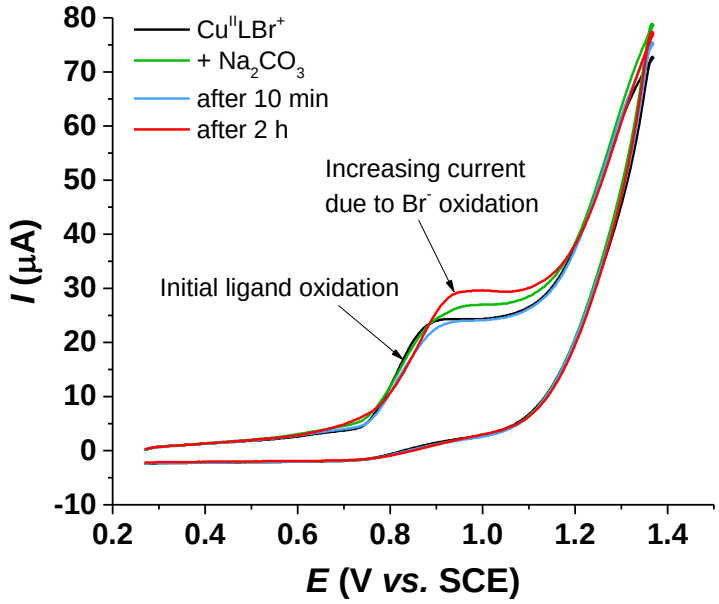


Figure S1. Cyclic voltammetry (CV) of 1 mM $CuBr_2$/TPMA in DMSO + 0.1 M Et_4NBF_4 in the absence (black) and presence of increasing amounts of Na_2CO_3. Recorded on a GC electrode, at scan rate 0.2 Vs^{-1}, T = 25 °C.

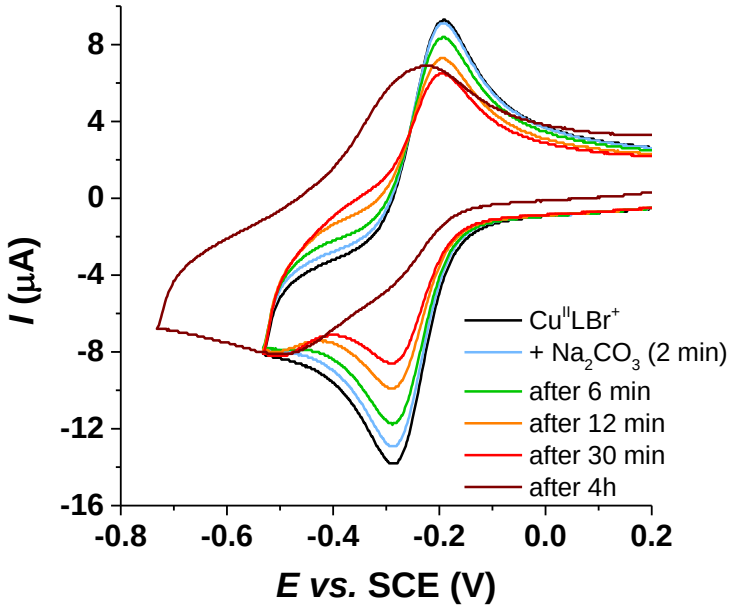


Figure S2. CV of 1 mM $CuBr_2$/TPMA in anhydrous DMSO + 0.1 M Et_4NBF_4 in the absence (black) and presence of 6.7 mM Na_2CO_3. Recorded on a GC electrode, at scan rate 0.2 Vs^{-1}, *T* = 25 °C.

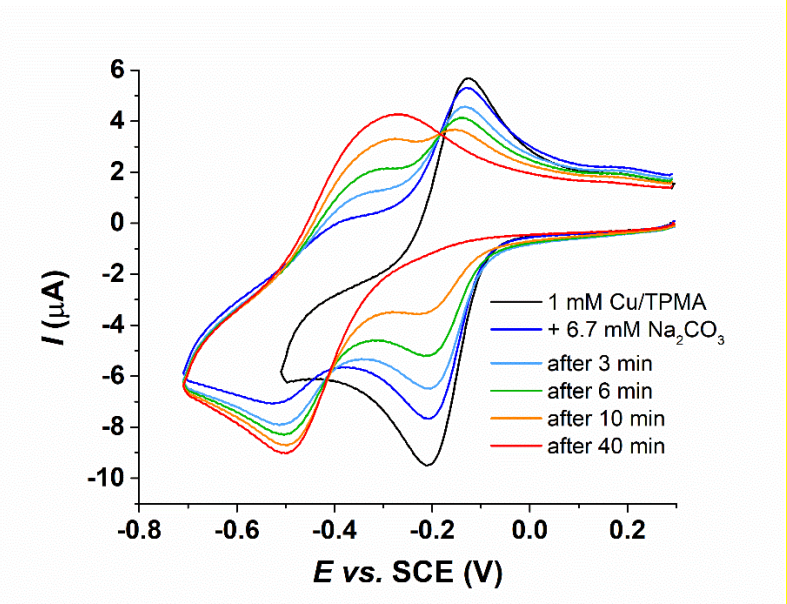


Figure S3. CV of 1 mM $Cu(OTf)_2$/TPMA in DMSO + 0.1 M Et_4NBF_4 in the absence (black) and presence of 6.7 mM Na_2CO_3. Recorded on a GC electrode, at scan rate 0.2 Vs^{-1}, *T* = 25 °C.

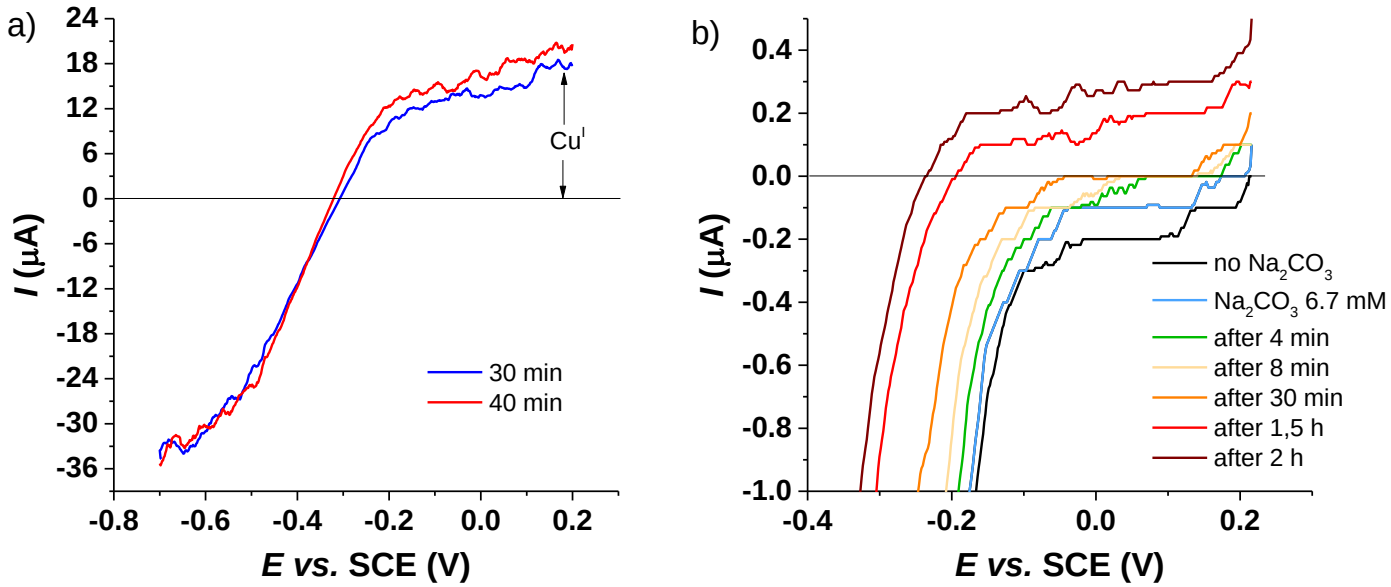
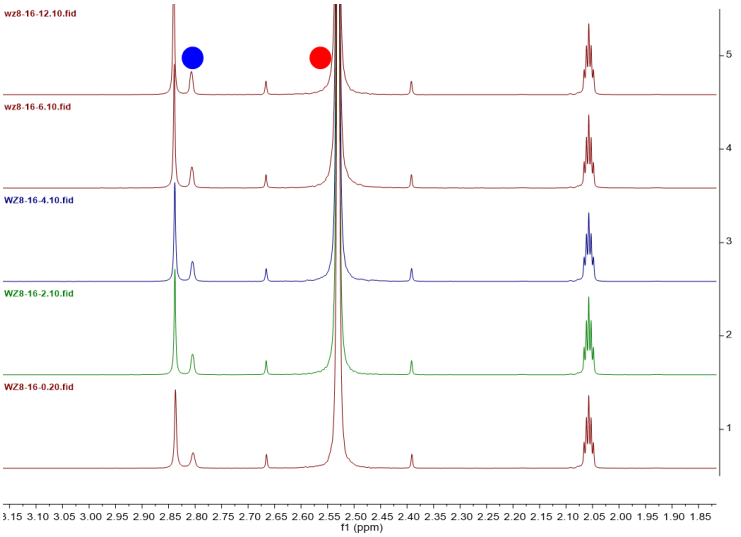


Figure S4. Linear sweep voltammetry recorded under a) ultrasound, and b) intense stirring at scan rate 0.01 Vs^{-1}, in DMSO + 0.1 M Et_4NBF_4, on1 mM $CuBr_2$/TPMA, before and/or after addition of 6.7 mM Na_2CO_3.



Time (h)	*Int* ●	*Int* ●
0	100	1.39
2	100	1.50
4	100	1.57
6	100	1.59
12	100	1.62

Figure S5. *In-situ* observation of DMSO in acetone-d6. $[DMSO]_0 = 150$ mM, $[CuBr_2]_0 = 15$ mM, $[TPMA]_0 = 60$ mM, $[Na_2CO_3]_0 = 45$ mM. Ultrasonic bath (25 $^oC \pm 5\ ^oC$, 40 kHz, 110 W). The initial presence of dimethyl sulfone is an impurity of the DMSO solvent.

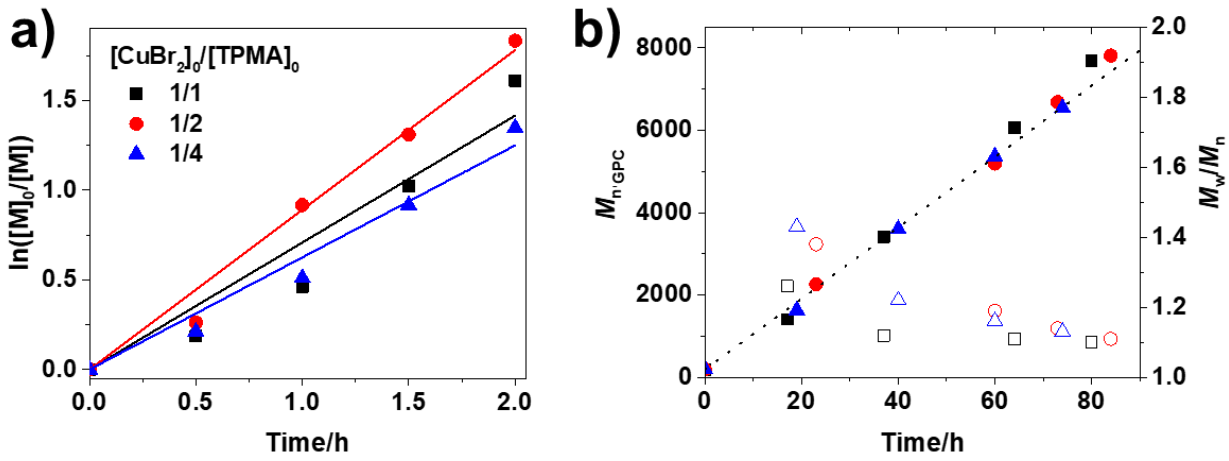


Figure S6. a) Kinetics of polymerization. b) Evolution of molecular weight and dispersity with conversion. Reaction conditions: $[MA]_0:[EBiB]_0:[CuBr_2]_0:[TPMA]_0$ = 100:1:0.015:X, 0.05 wt% Na_2CO_3 in 50% (v/v) DMSO. Ultrasonic bath (25 °C ± 5 °C, 40 kHz, 110 W).

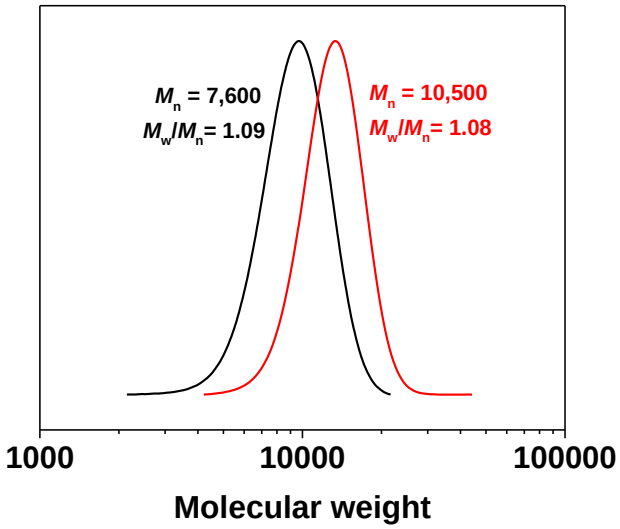


Figure S7. GPC traces for the chain extension of PMA-Br with MA.

Table S2. Results for sodium carbonate catalyzed ATRP with various ligands under ultrasound

Entry[a]	Ligand	$[CuBr_2]_0/[L]_0$	t (h)	Conversion[b]	$M_{n,th}$[c]	$M_{n,GPC}$[d]	M_w/M_n[d]
1	TPMA	1/1	2	80%	7080	7680	1.10
2	TPMA	1/2	2	84%	7420	7810	1.11
3	TPMA	1/4	2	74%	6559	6540	1.13
4	TPMA*	1/1	2	60%	5355	5250	1.19
5	Me6TREN	1/1	2	55%	4930	5180	1.10

[a]Reaction conditions: $[MA]_0:[EBiB]_0:[CuBr_2]_0:[L]_0:[Na_2CO_3]_0$ = 100:1:0.015:X:0.1 in 50% (v/v) DMSO. Ultrasonic bath (25 °C ± 5 °C, 40 kHz, 110 W). [b]Conversion determined by ^{1}H NMR. [c]Calculated on the basis of conversion (i.e., $M_{n,th} = M_{EBiB} + [MA]_0/[EBiB]_0 \times$ conversion $\times M_{MA}$). [d]Determined by GPC in THF, based on linear PMMA as calibration standard.

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Table S3. Results for the control experiments

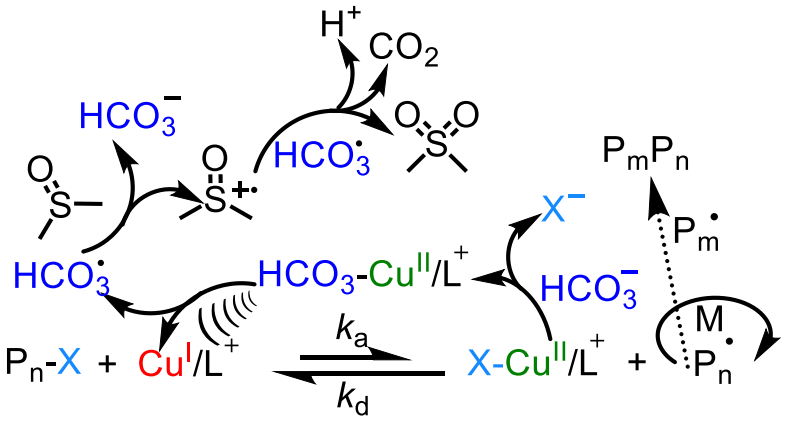
Entry	Stimuli	Na_2CO_3	*t* (h)	Conversion[a]	$M_{n,th}$[b]	$M_{n,GPC}$[c]	M_w/M_n[c]
1[d]	US	1000	2	0	N/A	N/A	N/A
2[e]	US	1000	20	0	N/A	N/A	N/A
3[e]	US	0	20	0	N/A	N/A	N/A
4[f]	US	1000	2	0	N/A	N/A	N/A

[a]Conversion determined by ^{1}H NMR. [b]Calculated on the basis of the conversion (i.e., $M_{n,th} = M_{EBiB} + [MA]_0/[EBiB]_0 \times \text{conversion} \times M_{MA}$). [c]Determined by GPC in THF, based on linear PMMA as calibration standard. [d]$[MA]_0$: $[CuBr_2]_0$:$[TPMA]_0$:$[Na_2CO_3]_0$ = 100: 0.015:0.06:0.1 in 50% (v/v) DMSO. [e]$[MA]_0$:$[DDMAT]_0$:$[Na_2CO_3]_0$ = 1000:1:1 in 50% (v/v) DMSO. [f]$[MA]_0$:$[EBiB]_0$:$[CuBr_2]_0$:$[TPMA]_0$:$[Na_2CO_3]_0$ = 100:1:0.015:0.06:0.1 in 50% (v/v) sulfolane. All the reactions were performed in an ultrasonic bath (25 °C ± 5 °C, 40 kHz, 110 W).

Table S4. Results for sono-ATRP using various carbonate salts

Entry[a]	DP_t	Salt	Concentration (ppm)	t (h)	*Conv.*[b]	$M_{n,th}$[c]	$M_{n,GPC}$[d]	M_w/M_n[d]
1	100	$NaHCO_3$	1000	2	83%	7333	6,300	1.10
2	100	K_2CO_3	1000	2	68%	6043	4,800	1.11
3	100	NH_4HCO_3	1000	2	40%	3635	3,800	1.13
4	200	NH_4HCO_3	1000	8	92%	16,214	14,800	1.06

[a]Reaction conditions: $[MA]_0:[EBiB]_0:[CuBr_2]_0:[TPMA]_0$ = 100:1:0.015:0.06 in 50% (v/v) DMSO. Ultrasonic bath (25 °C ± 5 °C, 40 kHz, 110 W). [b]Conversion determined by ^{1}H NMR. [c]Calculated on the basis of conversion (i.e., $M_{n,th} = M_{EBiB} + [MA]_0/[EBiB]_0 \times$ conversion $\times M_{MA}$). [d]Determined by GPC in THF, based on linear PMMA as calibration standard.



Scheme S1. Proposed mechanism of sono-ATRP in the presence of bicarbonate.