Supporting Information

Highly Efficient Atom Transfer Radical Polymerization System Based on the SaBOX/Copper Catalyst

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1. General Information

Unless stated otherwise, all manipulations with air- and moisture-sensitive chemicals and reagents were performed using standard Schlenk techniques on a dual-manifold line, or in an inert gas (N_2)-filled glovebox. All solvents and reagents were obtained from commercial sources and were purified according to standard procedures before use. All the monomers were purchased and dried over activated CaH_2 overnight, followed by vacuum distillation and stored in bottles at −22 °C inside of a freezer. ^{1}H NMR spectra were recorded on Varian 400 MHz spectrometer and Agilent Technologies 400 MHz spectrometer. The number-average molecular weight (M_n) and polydispersity index (Đ) were measured by gel permeation chromatography (GPC). The analysis was undertaken at 25 ºC with purified high-performance-liquid-chromatography-grade THF (for polymers of acrylate, methacrylate and styrene type monomers) or DMF (for poly(N,N-dimethylacrylamide)) or water (for poly(methacrylic acid)) as the eluent. Calibration was performed with standard PMMA (for polymers of acrylates and methacrylates as well as poly(N,N-dimethylacrylamide)), PS (for polymers of styrene type monomers) or PEG (for poly(methacrylic acid)). MALDI-TOF MS was conducted using a Shimadzu Axima Performance MALDI-TOF/TOF mass spectrometer, equipped with a nitrogen laser delivering 2 ns laser pulses at 337 nm with positive ion TOF detection performed using an accelerating voltage of 20 kV. Solutions in tetrahydrofuran (50 μL) of dithranol as a matrix (saturated solution), LiCl as the cationization agent (1.0 mg mL^{-1}) and sample (1.0 mg mL^{-1}) were mixed, and 0.7 μL of the mixture was applied to the target plate. The cyclic voltammetry measurements were done in accordance to the literature (*J. Am. Chem. Soc.*, **2008**, *130*, 10702) and recorded at 25 °C with a CHI660E potentiostat. Solutions of $CuBr_2$/L (1.0 mM) were prepared in dry CH_3CN containing 0.1 M Bu_4NPF_6 as the supporting electrolyte. Measurements were carried out under nitrogen at a scan rate of 0.1 V·s^{-1} using a glassy carbon disk as the working electrode and a platinum wire as the counter electrode. Potentials were recorded versus SCE using a 0.1

M Bu_4NPF_6 salt bridge. K_{ATRP} value was estimated through correlation to Figure 2 in literature (*J. Am. Chem. Soc.*, **2008**, *130*, 10702). The gas chromatography analyses were performed using Agilent 7890A, autosample, and a J&W Scientific DB-1701column (30×0.25×0.25) with an FID detector. The injector and detector temperature were kept constant at 280 °C. The temperature program for the GG column was as follows: initial temperature 45 °C, 2 min; ramp 5 °C/min; final temperature 180 °C,5 min. The UV-vis spectroscopic measurements were performed on a Shimadzu UV-2700 UV/vis spectrometer.

2. General ATRP Procedure

All polymerizations were set up and performed under an atmosphere of oxygen-free, dry argon using standard Schlenk-line techniques or inside a nitrogen-filled glovebox. In an ampule equipped with a magnetic stirrer bar, a mixture of $CuBr_2$, ligand and Cu(0) powder in solvent was stirred at room temperature for 2 h under the atmosphere of nitrogen. After that, monomer and initiator were added into the ampule. The ampules were placed at a certain temperature. After stirring for the allotted period of time, an aliquot (0.05 mL) was removed and quenched with $CDCl_3$ (0.5 mL). Conversion was determined by integration of the monomer vs. polymer resonances in the ^1H NMR spectrum of the crude product. After completion of the reaction, the contents of the ampules were dissolved in THF. The solution was filtered through a glass funnel with neutral alumina. The filtrate was concentrated under reduced pressure. The residuals were resolved with 5 mL THF. This solution was added to an approximately 50-fold excess of rapidly stirred methanol. The precipitate that formed was filtered and washed with methanol. The precipitate was dried to constant weight in a vacuum oven at 50 ^oC.

3. The SARA ATRP of MMA Employing Different Ligands and Initiators

Table S1. The SARA ATRP of MMA Employing Different Ligands and Initiators[a]

Run	L	Initiator	t (h)	Conv.[b] (%)	$M_{n,\ theory}$ (kg/mol)	$M_{n,GPC}$ (kg/mol)	Đ
1	SaBOX	EBiB	3.0	75	7.7	29.0	1.52
2	SaBOX	EBPA	2.3	74	7.7	30.2	1.59
3	PMDETA	EBiB	3.0	6.2	0.7	141.3	2.14
4	PMDETA	EBPA	2.3	2.9	0.4	505.3	1.56
5	Me_6TREN	EBiB	3.0	0	–	–	–
6	Me_6TREN	EBPA	2.3	0	–	–	–

[a] Reaction conditions: n(MMA):n(Initiator):n($CuBr_2$):n(SaBOX):n(Cu(0)) = 200:2:1:2:4, DMSO was used as the solvent (50% V_{total}), 25 °C, DP_{target} = 100. [b] Monomer conversion measured by ^{1}H NMR.

4. The SARA ATRP of MMA with DP_{target} = 100 in IPA/DMSO Mixed Solvent

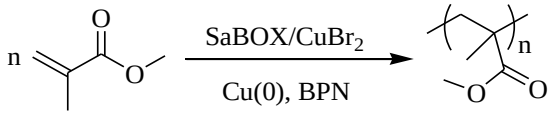
Table S2. The SARA ATRP of MMA with DP_{target} = 100 in IPA/DMSO Mixed Solvent[a]

Run	IPA/DMSO (V/V)	t (h)	Conv.[b] (%)	$M_{n,\ theory}$ (kg/mol)	$M_{n,\ GPC}$ (kg/mol)	Đ
1	1/1	3.0	88	8.9	15.3	1.23
2	2/1	5.0	90	9.1	16.6	1.26
3	5/1	6.0	90	9.1	15.8	1.18
4	7/1	6.5	90	9.1	11.9	1.19
5	10/1	10	88	8.9	9.2	1.17

[a] Reaction conditions: n(MMA):n(BPN):n($CuBr_2$):n(SaBOX):n(Cu(0)) = 200:2:1:2:4, n(MMA) = 5 mmol, IPA/DMSO was used as the solvent (50% V_{total}), 25 °C, DP_{target} = 100. [b] Monomer conversion measured by ^{1}H NMR.

5. First-Order Kinetic Plots as well as Evolution of MW and Đ as a Function of Monomer Conversion for ATRP of MMA

Table S3. First-Order Kinetic Study and Evolution of MW and Đ as a Function of Monomer Conversion for ATRP of MMA[a]



Run	t (h)	conv.[b] (%)	$M_{n,GPC}$ (kg/mol)	$M_{n,theory}$ (kg/mol)	Đ	$\ln(C^0_M/C_M)$
1	0.5	14	2.1	1.5	1.33	0.1586
2	1	18	3.7	1.9	1.18	0.1985
3	1.5	24	4.1	2.5	1.19	0.2744
4	2	35	4.3	3.6	1.35	0.4308
5	3	48	5.4	4.9	1.40	0.6539
6	4	53	6.3	5.4	1.29	0.7550
7	5	58	5.8	5.9	1.35	0.8675
8	6	70	7.7	7.1	1.27	1.2040
9	7	81	9.7	8.2	1.28	1.6607

[a] Reaction conditions: n(M):n(Initiator):n($CuBr_2$):n(Ligand):n(Cu(0)) = 200:2:1:2:4, n(M) = 5 mmol, IPA/DMSO (7/1 (v/v)) was used as the solvent (50% V_{total}), 25 °C. [b] Monomer conversion measured by ^{1}H NMR.

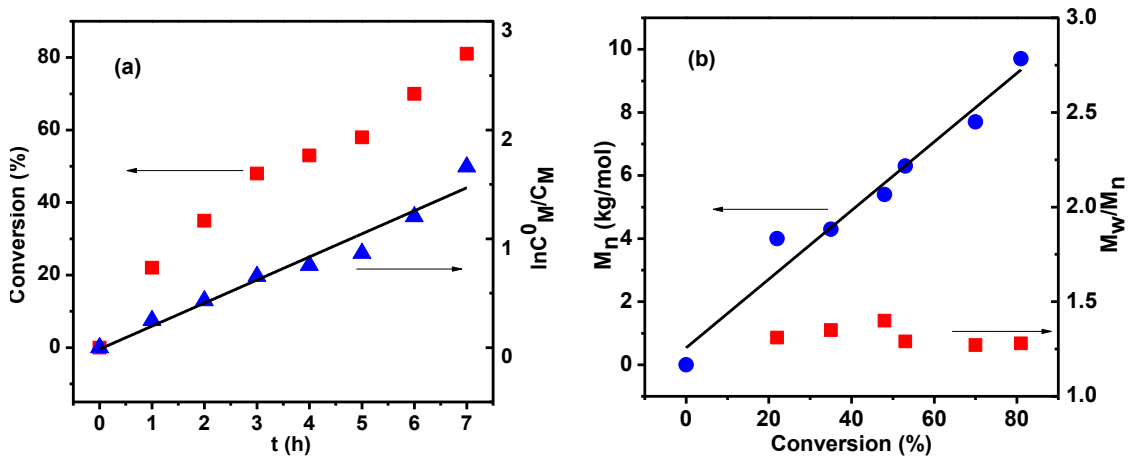


Figure S1. (a) First-order kinetic plot as well as (b) evolution of MW and Đ (M_w/M_n) as a function of conversion for ATRP of MMA employing SaBOX as the ligand (Table S2).

6. The GPC Traces of PMMA with Different DP_{target}s

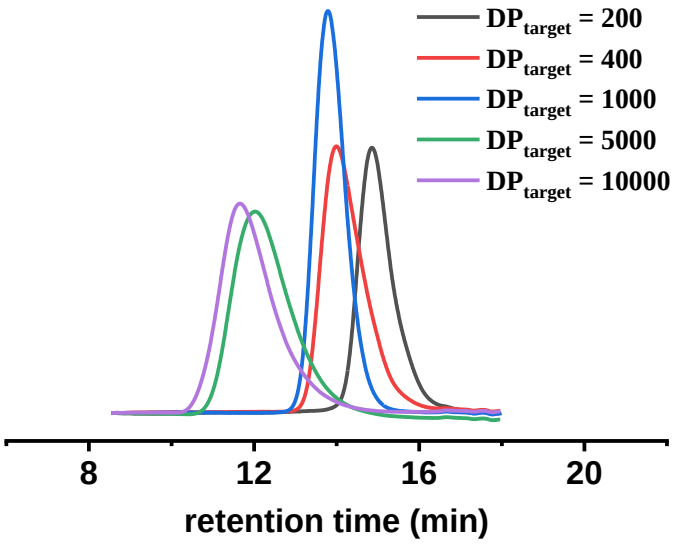


Figure S2. GPC traces of PMMA (DP_{target} = 200-10000, runs 5 and 7-10 in Table 2)

7. MALDI-TOF Mass Spectrum of PMMA

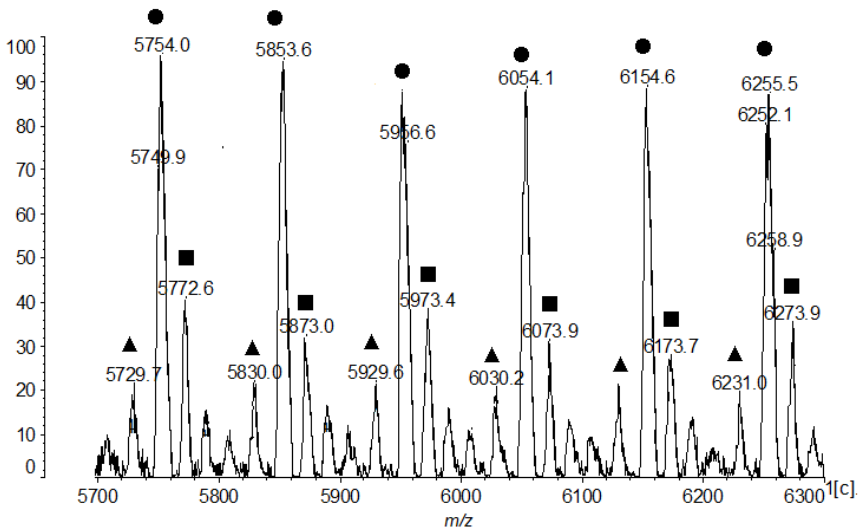


Figure S3. MALDI-TOF mass spectrum of PMMA produced by SaBOX/$CuBr_2$ (M_n = 4.3 kg/mol, Đ = 1.21). ▲: $CN(CH_3)CH(MMA)_nBrH^+$, ●: $CN(CH_3)CH(MMA)_nBrNa^+$, ■: $CN(CH_3)CH(MMA)_nBrK^+$.

8. In Situ Chain Extension Experiments

Table S4. Conversion and MW Analysis of the in situ Chain Extension of Poly(methyl methacrylate)

Run	Block	DP_{target}	t (h)	Conv. (%) [c]	$M_{n,\ GPC}$ (kg/mol)	$M_{n,theory}$ (kg/mol)	Đ
1[a]	MMA	50	16	>99	7.0	5.1	1.21
2[b]	MMA-MMA	50	8	75	13.2	8.8	1.12

[a] Reaction conditions: n(MMA):n(BPN):n($CuBr_2$):n(SaBOX):n(Cu(0)) = DP_{target}:1:0.5:1:2, n(MMA) = 2.5 mmol, IPA/DMSO (7/1 (v/v)) was used as the solvent (50% V_{total}), 25 ºC. [b] in situ adding MMA and solvent with a ratio of 1:1 (V/V). [c] Monomer conversion measured by ^{1}H NMR.

Table S5. The Synthesis of PMMA-*b*-P*n*BMA via in situ Chain Extension

Run	Block	DP_{target}	t (h)	Conv. [c] (%)	$M_{n,\ GPC}$ (kg/mol)	$M_{n,theory}$ (kg/mol)	Đ
1[a]	MMA	50	15	99	7.3	5.1	1.17
2[b]	MMA-*n*BMA	50	12	86	13.0	11.2	1.15

[a] Reaction conditions: n(MMA):n(BPN):n($CuBr_2$):n(SaBOX):n(Cu(0)) = DP_{target}:1:0.5:1:2, n(MMA) = 2.5 mmol, IPA/DMSO (7/1 (v/v)) was used as the solvent (50% V_{total}), 25 ºC. [b] in situ adding *n*BMA and solvent with a ratio of 1:1 (V/V). [c] Monomer conversion measured by ^{1}H NMR.

9. The Determinations of Equilibrium Constant and Activation Rate Constant

$$F(\mathrm{Y}) = \left(\frac{I_0 C_0}{C_0 - I_0}\right)^2 \left(\frac{1}{C_0^2(I_0 - Y)} + \frac{2}{I_0 C_0 (C_0 - I_0)} \ln\left(\frac{I_0 - Y}{C_0 - Y}\right) + \frac{1}{I_0^2 (C_0 - Y)}\right)$$

Equation S1. Modified Fischer's Equation

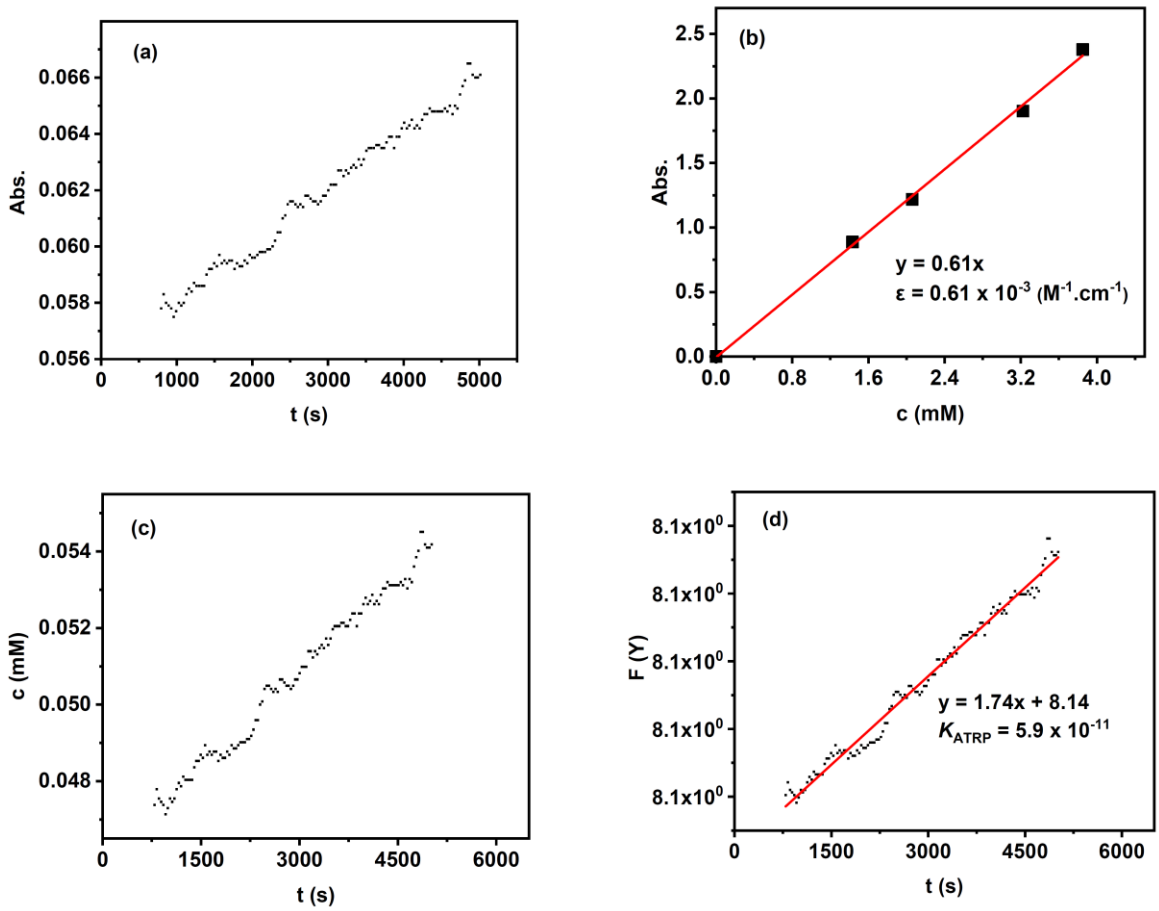


Figure S4. (a) The absorbancy of Cu(II) species varying with time; (b) The determination of absorption coefficient; (c) The concentration of Cu(II) species varying with time; (d) Experiment for the determination of K_{ATRP} via new equations (F(Y) vs t): $[CuBr]_0 = [SaBOX]_0 = 5$ mM, $[EBiB]_0 = 500$ mM; Solvent = MeCN; temperature = 25 ± 2 °C.

$$\text{pseudo-1}^{\text{st}}\text{-order: } \left[\frac{\text{Cu}^{\text{I}}\text{Y}}{\text{L}_{\text{n}}}\right]_0 \gg [R\text{-}X]_0$$

$$-\frac{d\ln[R-X]}{dt} = \text{slope} = k_{\text{app}}[\text{Cu}^{\text{I}}\text{Y}/\text{L}_{\text{n}}]_0 = k_{\text{a}}[\text{Cu}^{\text{I}}\text{Y}/\text{L}_{\text{n}}]_{\text{act}}$$

Equation S2. Pseudo-first-order Equation

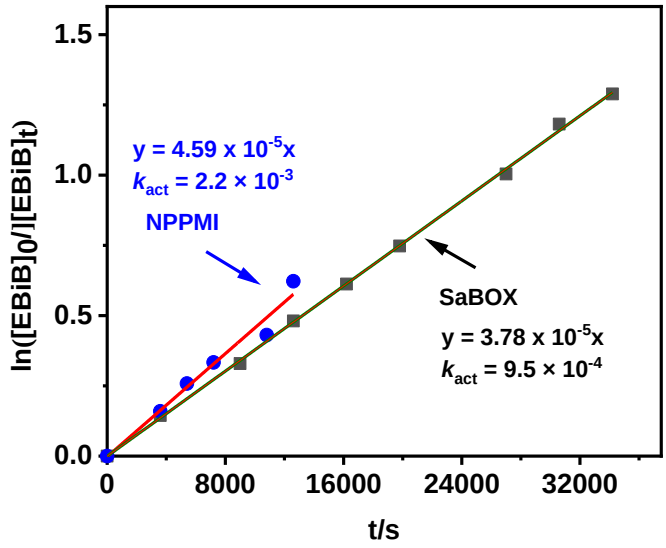


Figure S5. Pseudo-first-order kinetic plot of the activation process for SaBOX and NPPMI in acetonitrile at 35 °C; $[CuBr]_0/[EBiB]_0/[TEMPO]_0/[TCB]_0$ = 20/1/10/2, $[CuBr]_0$ = $[Ligand]_0$ = 40 mM.

Table S6. Experimental Determination of activation rate constants[a]

Run	Ligand	Slope (10^{-5} S^{-1})	k_{app} ($M^{-1}\cdot S^{-1}$)	k_{act} ($M^{-1}\cdot S^{-1}$)
1	NPPMI	4.59	1.1×10^{-3}	2.2×10^{-3}
2	SaBOX	3.78	9.5×10^{-4}	9.5×10^{-4}

[a] Conditions: $[CuBr]_0/[EBiB]_0/[TEMPO]_0/[TCB]_0$ = 20/1/10/2, $[CuBr]_0$ = $[Ligand]_0$ = 40 mM; Solvent = MeCN; temperature = 35 ± 2 °C.

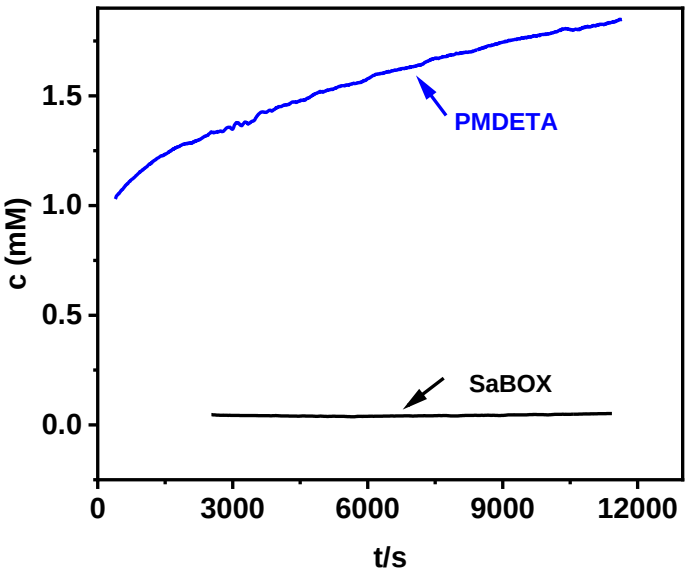


Figure S6. The evolution of Cu(II) species by the UV-vis spectrometric experiments: $[CuBr]_0 = [Ligand]_0 = [BPN]_0 = 5$ mM; Solvent = MeCN; temperature = 25 ± 2 °C.