Schiff Base Ligand for Photoinduced Atom Transfer Radical Polymerization

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Experimental Section

Materials

Tris[*N*-(2-pyridylmethyl)-2-iminoethyl]amine (Py$_3$Tren) and *N*-ethyl-2-pyridylmethanimine (PyEthyl) were synthesized according to literature procedures and stored at 2-8 °C.[1, 2] Copper(II) trifluoromethanesulfonate (Cu^{II}(OTf)$_2$, 98%, Energy Chemical), dimethyl sulfoxide (DMSO, 99%, Aladdin), ethyl α-bromoisobutyrate (EBiB, 98%, TCI), methyl methacrylate (MMA, >99.5%, Aladdin) were used as received. All other reagents and solvents were obtained from Aladdin (China) and used without further purification unless otherwise stated.

Instruments and analysis

^{1}H NMR spectra were recorded at 25 °C with a Bruker AV 500 M spectrometer using deuterated solvents obtained from Aladdin. The number-average molecular weight (M_n) and the molecular weight distribution (M_w/M_n) were determined by Waters 1515 size exclusion chromatography (SEC) in N,N-dimethylbenzamide (DMF) at 40 °C with a flow rate of 1.00 mL min^{-1}. The SEC was equipped with refractive index (RI) and UV detectors, a 20 μm guard column (4.6 mm × 30 mm, 100–10 K) followed by three Waters Styragel columns (HR1, HR3 & HR4) and an autosampler. Narrow linear polystyrene standards in the range of 540 to 7.4 × 10^5 g mol^{-1} were used to calibrate the system. All samples were passed through a 0.45 μm PTFE filter before analysis. A 120W super strong ultraviolet low pressure mercury lamp (CEL-LPH120-254, Beijing China Education Au-light co., Ltd.) and a 300 W Xe lamp (CEL-HXF 300, Beijing China Education Au-light co., Ltd.) with a 400 nm cutoff filter was

used as light source. The optical transmittance of the aqueous solution of thermoresponsive polymers at a wavelength of 500 nm was acquired on a SHIMADZU UV-2600 UV/Vis spectrophotometer. Electrospray ionization mass spectrometry (ESI-MS) measurements were performed in positive mode through using a Bruker Esquire 3000 Plus instrument.

General procedures for the photoinduced polymerization of MMA

MMA (2.3 mL, 22 mmol, 50 eq), EBiB (65 µL, 0.44 mmol, 1 eq), CuBr$_2$ (7.1 mg, 31.7 µmol, 0.072 eq), Py$_3$Tren (65.5 mg, 158.4 µmol, 0.36 eq) and DMSO (2.3 mL) were added to a vial with a rubber seal and magnetic stir bar and degassed by purging with nitrogen for 30 mins. The reaction mixture was placed in a photoreactor, irradiating at different radiation sources (UV lamp or visible light), and monitored by taking samples periodically, analysing the polymer by both SEC and ^{1}H NMR spectroscopy.

**General procedures for *in-situ* chain extension reactions**

MMA (2.3 mL, 22 mmol, 50 eq), EBiB (65 µL, 0.44 mmol, 1 eq), CuBr$_2$ (7.1 mg, 31.7 µmol, 0.072 eq), Py$_3$Tren (65.5 mg, 158.4 µmol, 0.36 eq) and DMSO (2.3 mL) were added to a vial with a rubber seal and magnetic stir bar and degassed by purging with nitrogen for 30 mins. The reaction mixture was placed in a photoreactor, irradiating at visible light. After 10 h a 1: 1 mixture of degassed MMA (50 eq) and DMSO was added to the reaction mixture via degassed syringe. Samples were taken periodically and conversions were measured using ^{1}H NMR and SEC analysis.
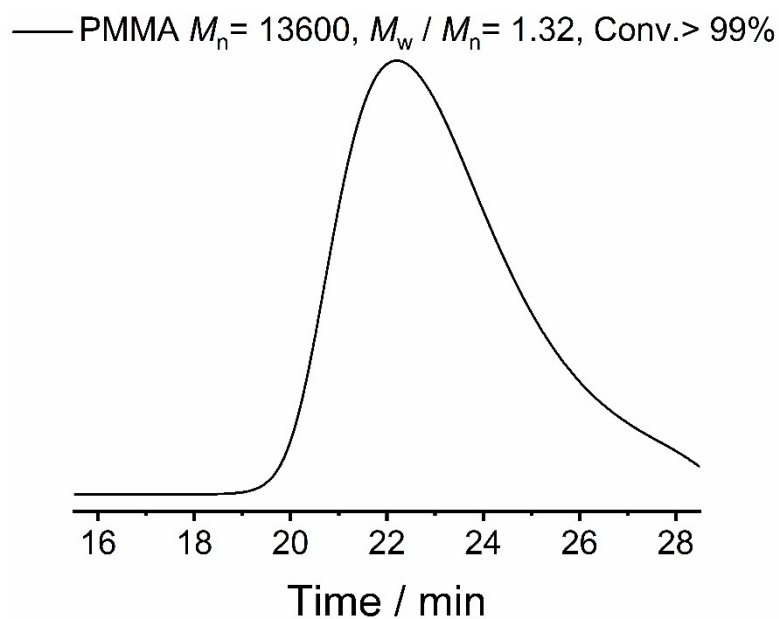
Figure S1. SEC elution curve of poly(MMA).
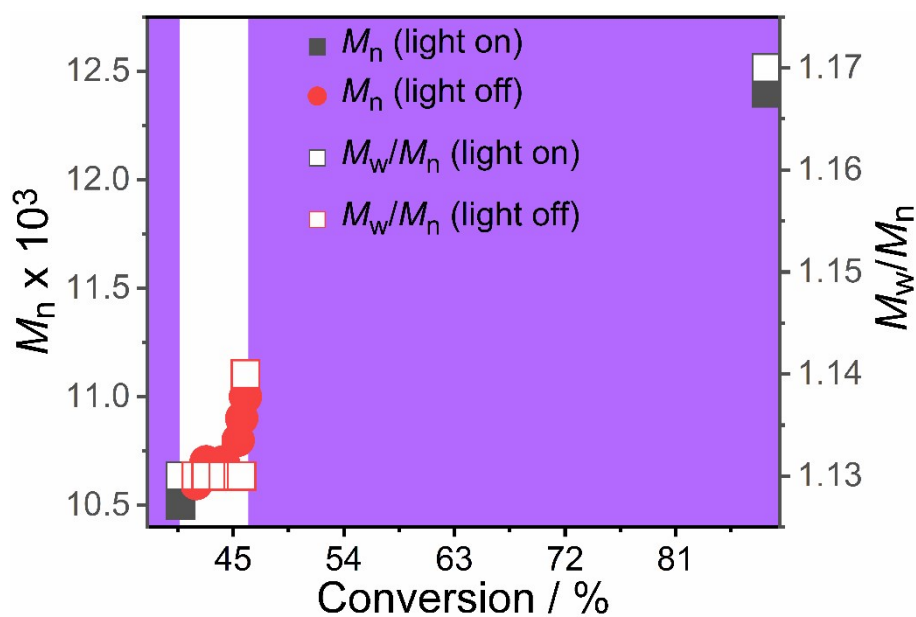
Figure S2. Temporal control of the Photo-ATRP of MMA under visible light irradiation. Molecular weight and dispersity as a function of monomer conversion. Reaction conditions: $[MMA]_0:[EBiB]_0:[CuBr_2]_0:[Py_3Tren]_0 = 50:1:0.072:0.36$ in 50 vol% DMSO with visible light radiation.
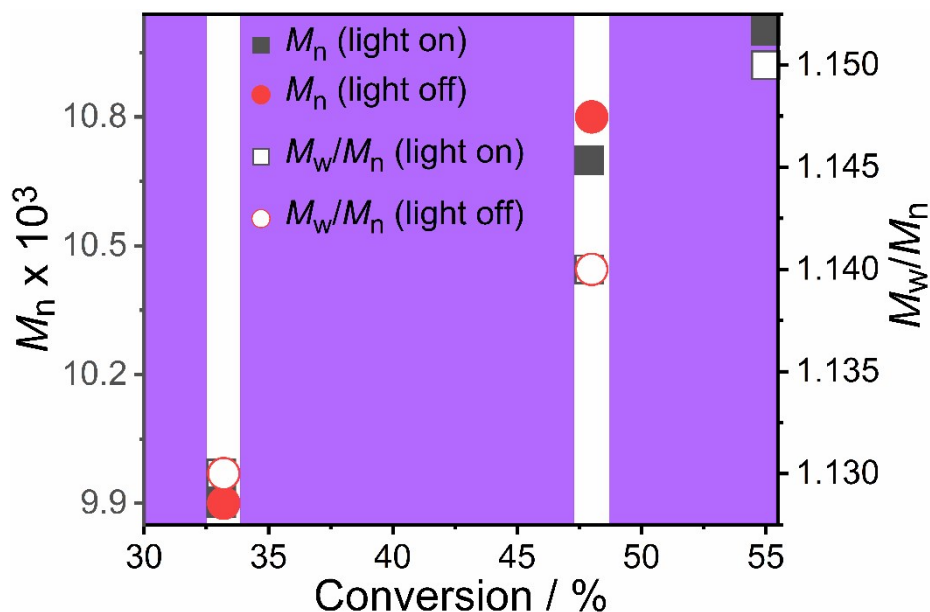
Figure S3. Temporal control of the Photo-ATRP of MMA under visible light irradiation. Molecular weight and dispersity as a function of monomer conversion. Reaction conditions: $[MMA]_0:[EBiB]_0:[CuBr_2]_0:[Py_3Tren]_0 = 50:1:0.072:0.288$ in 50 vol% DMSO with visible light radiation.
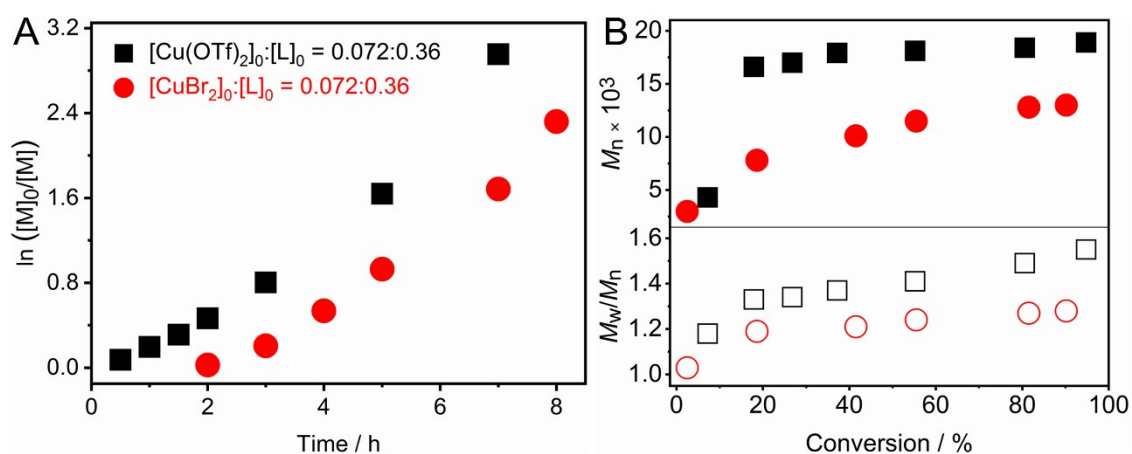

Figure S4. (A) Kinetics of polymerization (B) evolution of the M_n and M_w/M_n with conversion. Conditions: $[MMA]_0:[EBiB]_0:[Cu^{II}]_0:[Py_3Tren]_0 = 50:1:0.072:0.36$, in DMSO, irradiated by visible light. Two different Cu^{II} salts were used, $CuBr_2$ and $Cu^{II}(OTf)_2$.
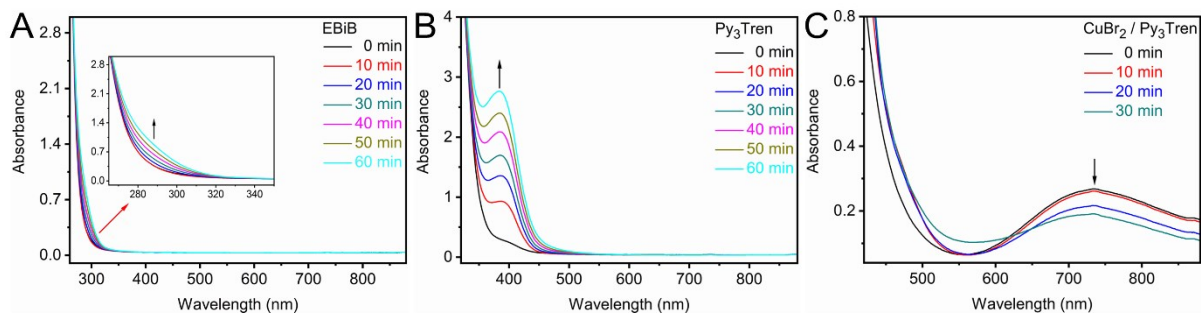
Figure S5. Evolution of UV−Vis spectra as a function of time. Conditions: (A) [EBiB] = 22 mM, (B) [L] = 4.4 mM, (C) [CuBr$_2$] = 2.2 mM, [L] = 2.2 mM, where L= Py$_3$Tren in DMSO. In all cases the samples were irradiated with 254 nm radiation, at 25 ºC.
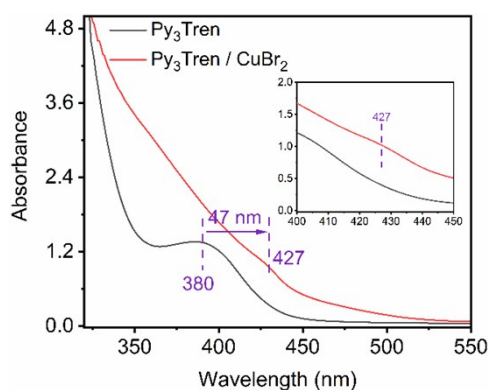
Figure S6. Evolution of UV−Vis spectra as a function of time. Conditions: [L] = 4.4 mM, [CuBr$_2$ / L] = 2.2 mM, where L= Py$_3$Tren in DMSO at 25 ºC.
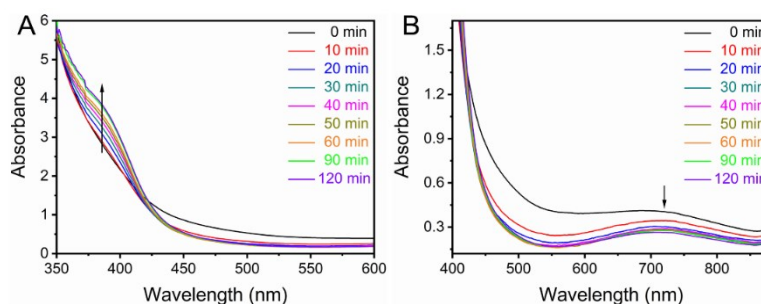
Figure S7. A partial enlarged view of the evolution of UV/Vis spectra as a function of time. Conditions: [CuBr$_2$] = 2.2 mM, [L] = 11 mM, where L= Py$_3$Tren in MMA/DMSO = 1/1 (v/v). In all cases the samples were irradiated with 254 nm radiation, at 25 ºC.

Table S1. Photo-ATRP of MMA to range of DP_n.

Entry	$[M]_0:[I]_0:[CuBr_2]_0:[L]_0$ [a]	Time / h	$M_{n, th}$	$M_{n, SEC}$ [b]	M_w / M_n [b]	Conv. [c]
1	50 : 1 : 0.072 : 0.36	10	5100	13800	1.33	97
2	100 : 1 : 0.072 : 0.36	16	9600	22000	1.26	94
3	150 : 1 : 0.072 : 0.36	23	13700	27200	1.29	90

[a] M = MMA, I = EBiB, L = Py_3Tren, DMSO (50%, v/v), irradiated by visible light; [b] by SEC; [c] by ^1H NMR spectroscopy.

Table S2. Comparison of theoretical and experimentally determined molecular mass for the significant structures found for various reagent compositions.

Structure	DP (n)	$(m/z)_{theo}$[a]	$(m/z)_{exp}$[b]
$[MMAH + Na]^+$	2	325.16	325.00
$[MMAH + H]^+$	4	503.28	503.03
$[MMAH + Na]^+$	4	525.27	525.32
$[Py_3TrenH + Na]^+$	1	536.27	536.15
$[Py_3TrenH + H]^+$	2	614.34	614.29
$[Py_3TrenH + Na]^+$	2	636.33	636.26
$[Py_3TrenH + Na]^+$	3	736.38	736.34
$[Py_3TrenH + H]^+$	4	814.44	814.38
$[EH + Na]^+$	4	539.28	539.31
$[EH + Na]^+$	5	639.34	639.27
$[EH + H]^+$	6	717.40	717.35
$[EBr + H]^+$	4	595.20	595.13
$[EE + Na]^+$	4	653.35	653.43
$[EE + Na]^+$	7	953.51	953.44
$[BrH + H]^+$	5	581.19	581.21
$[BrH + H]^+$	8	881.35	881.11

[a]Calculated exact mass. [b]Measured by ESI-MS.

REFERENCES

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2. X. Xu, C. Bao, M. Hong, D. Li and Q. Zhang, *Polym. Chem.*, 2020, **11**, 6356-6364.